

SPECIFICATION

TITLE OF THE INVENTION

"ELECTROCHEMICAL DEVICE AND GAS STORAGE DEVICE"

CROSS REFERENCES TO RELATED APPLICATIONS

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The present application claims priority to Japanese Patent Document Nos. P2002-009456 filed on January 18, 2002, and P2002-373798 filed December 25, 2002, the disclosures of which are herein incorporated by reference.

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BACKGROUND OF THE INVENTION

The present invention relates to a pressure reducing device, an electrochemical device, a pressure reducing and pressurizing device, a gas storage device, a gas storage assist system, and a method for driving these devices.

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To convert high pressure gas into low pressure gas, a mechanical gas regulator has been widely employed. The usual gas regulator has been a mechanical device as disclosed in, for instance, Japanese Patent Application Laid-Open No. H04-244506.

Now, according to the contents described in the Japanese Patent Application Laid-Open No. H04-244506, the usual gas regulator will be described below.

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The usual gas regulator is formed as shown in Fig. 1. That is, on one end of an inlet side of a main body case 86, an inlet pipe 87 is mounted. On the other end, an outlet port 88 is formed. To an opening part 86a formed on the upper surface of the main body case 86, a cover 89 is fixed. Between the main body case 86 and the cover 89, the peripheral edges of a diaphragm 90 are fixed. The diaphragm 90 air-tightly partitions an atmospheric pressure chamber 91 of the cover 89 side and a pressure reducing chamber 92 in the case 86.

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In the center of the diaphragm 90, an operating rod 93 vertically passes. The diaphragm 90 is sandwiched in and fixed between a collar part 93a provided in the operating rod 93 and a nut 94 screwed to an upper end of the operating rod 93. A spring 95 is interposed between the diaphragm 90 and the cover 89 to constantly urge the diaphragm. To the lower part of the operating rod 93, the operating end of an operating lever 96 is cross-linked so as to slide. The operating lever 96 is

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supported by the case 86 through a support shaft 97 so as to rotate. An operating end of the operating lever 96 is engaged with a valve body 98 that is opposed to an end nozzle part 87a of the inlet pipe 87 through an operating pin 99. In the cover 89, a vent hole 89a communicating with an atmospheric side is formed.

5 In the usual gas regulator constructed as described above, when an amount of gas consumed in a combustion device (not shown) is reduced to raise pressure in the pressure reducing chamber 92, the diaphragm 90 overcomes the urging force of the spring 95 to be displaced to the atmospheric pressure chamber 91 side, raise the operating rod 93 and rotate the operating lever 96 counterclockwise on the support
10 shaft 97. The valve body 98 is allowed to come near to the nozzle part 87a. Thus, an amount of inlet of gas is decreased to lower gas pressure in the pressure reducing chamber 92. In such a way, the gas pressure in the pressure reducing chamber 92 is maintained to a substantially constant value correspondingly to the urging force of the spring 95.

15 Accordingly, when high pressure gas (a gaseous material) is supplied from the inlet pipe 87 side, the gas of prescribed low pressure can be obtained in the outlet port 88 side.

 The usual gas regulator according to the above-described mechanical system has a large form in structural point of view. Further, since the above-
20 described gas regulator has movable parts, an abrasion due to a friction is generated so that the life of a machine is shortened. Further, noise is undesirably generated during an operation.

 Further, the usual gas regulator merely intends to reduce the pressure of gas and is only provided with a pressure reducing mechanism. Thus, a pressurizing
25 mechanism needs to be provided separately from the pressure reducing mechanism in order to apply pressure.

SUMMARY OF THE INVENTION

 The present invention relates to a pressure reducing device, an
30 electrochemical device, a pressure reducing and pressurizing device, a gas storage device, a gas storage assist system, and a method for driving these devices.

In an embodiment, the present invention provides a new pressure reducing device, an electrochemical device, a pressure reducing and pressurizing device, a gas storage device and a gas storage assist system, and a method for driving these devices that can solve problems typically associated with the conventional and
5 proposed device for converting high pressure gas to low pressure gas as described above.

In another embodiment, the present invention provides a compact, durable and silent pressure reducing device, an electrochemical device, a pressure reducing and pressurizing device, a gas storage device and a gas storage assist system, and a
10 method for driving these devices.

The present invention concerns in an embodiment a gas pressure regulator including an electrochemical cell including a first electrode for decomposing gas into ions, a second electrode for converting the ions generated in the first electrode into the gas again, and an ion conductor sandwiched in between both the electrodes;
15 and a high pressure vessel disposed in one side of the electrochemical cell.

The present invention concerns in an embodiment a gas pressure regulating method including a decomposing step of decomposing gas into ions in a first electrode; a conducting step of conducting the decomposed ions to a second electrode side through an ion conductor sandwiched in between the first electrode
20 and the second electrode; and a converting step of converting the conducted ions to the gas again in the second electrode.

In the gas pressure regulator and the gas pressure regulating method according to an embodiment of the present invention, since the decomposing step, the conducting step and the converting step are included and a mechanical movable
25 part is not provided in the device, a compact, durable and virtually silent gas pressure regulator can be realized.

Here, when the gas pressure regulator according to an embodiment of the present invention is driven, for instance, the electrochemical cell can function to reduce pressure in the high pressure vessel.

The electrochemical cell functions to reduce or increase the pressure in the high pressure vessel, so that the gas pressure regulator according to the present invention can operate as a pressure reducing and pressurizing device.

5 In these cases, since a mechanical movable part is not provided in the gas pressure regulator according to the present invention, a compact, durable and silent device can be obtained. According to an embodiment of the present invention, since one device is formed so as to have a pressure reducing mechanism and a pressure applying mechanism, a more compact device than a usual gas regulator can be realized.

10 In the present invention, gas is desirably in a state of gas under ordinary temperature and ordinary pressure. Specifically, the gas is desirably hydrogen gas, oxygen gas or the like according to an embodiment.

The ion conductor is preferably a film made of an electrolyte material capable of permeating ionized gas. Further, the first electrode and the second
15 electrode are preferably electrode films on which a catalyst such as platinum capable of ionic equilibrium of gas is carried in an embodiment.

In an embodiment, the electrode preferably has a heat resistance and a large surface area as much as possible. Each electrode can preferably come into tight contact with the ion conductor over an entire surface through the catalyst carried on
20 a surface. The electrode preferably has flexibility to some degree so as to come into tight contact with the ion conductor. Further, the electrode is preferably an activated electrode.

Accordingly, the first electrode and the second electrode are preferably porous or mesh shaped in an embodiment. For instance, the first electrode and the
25 second electrode can be formed in such a way that carbon fibers or porous carbons are formed in a sheet shape and an active catalyst is carried on a side which comes into tight or intimate contact with the ion conductor made of the sheet shaped electrode material. To such a sheet shaped electrode material, a net shaped core material formed by braiding metal wires, as a core material, may be inserted or
30 stuck. The metallic core material is inserted or stuck to the electrode so that the

electric conductivity of the electrode itself can be improved and a uniform current distribution over an entire surface can be expected.

The catalyst is desired to be fine particles of, for instance, platinum, ruthenium oxide, iridium oxide, and the like in an embodiment. Any other suitable
5 electrode materials such as silver by which a reaction as a purpose of the present invention proceeds may be employed.

The catalyst may be carried on the electrode by an ordinary method. For instance, a method may be used that a catalytic material or its precursor is carried on the surface of carbon powder, subjected to a process such as heating to form
10 catalytic particles and the catalytic particles are baked together with a fluororesin on the surface of the electrode. Further, an electrode body on which the catalytic material is not carried is previously formed. Then, a precursor of the catalytic material, for instance, the mixed aqueous solution of platinic chloride and ruthenium chloride or butyl alcohol solution is applied to the surface of the
15 electrode as application liquid and sintered in a reducing atmosphere including hydrogen at about 200°C to about 350°C. Thus, an alloy of platinum and ruthenium can be formed on the surface of the electrode pursuant to an embodiment.

The device according to an embodiment of the present invention has
20 preferably a low pressure vessel in the other side of the electrochemical vessel. The electrochemical cell preferably serves as a gas partition. The pressure is regulated by controlling a potential between both the electrodes is preferably provided when a pressure difference is generated at both the sides of the electrochemical cell. Further, an electromotive force generated from the pressure difference is preferably
25 short-circuited by a relay, or the like or pressure is preferably regulated by a variable resistor.

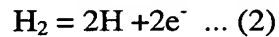
Ordinarily, when the pressure difference is generated at both the sides of the electrochemical cell, the electromotive force is generated from the pressure difference. This is known as the formula of Nernst including the term of pressure
30 shown in a below-described formula:

$$E = E_0 + (RT/2F) \ln(P_1/P_2) \dots (1)$$

In the formula (1), E_0 represents an ionized potential of gas, R represents a gas constant, T represents a temperature, F represents a Faraday constant, and P_1 and P_2 represent gas pressure.

Essentially, when the gas pressure is the same at both the sides of the electrochemical cell as the partition wall, a potential difference is not generated. However, when gas pressure in one side is raised, the electromotive force due to the term of $\ln(P_1/P_2)$ in the formula (1) is generated.

For instance, when the gas is hydrogen gas, equilibrium as shown by a below-described formula (2) exists on the catalyst such as platinum carried on the electrode.



When the pressure rises, this electrochemical equilibrium shifts to mitigate a stress. This reaction equilibrium causes a volume to be changed, which has a very important meaning. That is, when the pressure rises, the equilibrium shifts rightward so as to mitigate it. Thus, many electrons flow into the electrode to raise the potential. At the same time, many protons (H^+) are injected to the ion conductor in the high pressure vessel side so that the protons are apt to be diffused to the low pressure vessel side.

When the protons diffused to the low pressure vessel side are not recombined to the electrons, the protons cannot return to the hydrogen gas. Accordingly, when an electrical short-circuit in which the potential difference between both the electrodes is constant is generated, the protons are recombined to the electrons in the low pressure vessel side. Thus, apparently, the hydrogen gas flows to the low pressure vessel side.

In this process, the gas interrupting characteristics of the ion conductor is required. As described below, for instance, when the hydrogen gas is used as the gas, a proton conductor including fullerene or the like as a base is useful for the ion conductor.

Basically, since only ions of specific gas can pass through the ion conductor, the electrochemical cell also has a function as a gas refining filter. Accordingly, when the hydrogen gas is used as the gas, the electrochemical cell is

most suitable as a regulator for supplying the hydrogen gas to an electrochemical device such as a fuel cell under prescribed pressure.

As described above, the essence of the present invention resides in the formula of Nernst depending on pressure, that is, the above-described formula (1).

5 When the pressure difference is generated between both the electrodes, the potential of both the electrodes can be short-circuited by a relay, or the like, or the potential of both the electrodes can be controlled by a variable resistor to regulate the pressure.

Both the sides of the electrochemical cell serving as the gas partition wall
10 have closed vessels. When one side serves as a high pressure gas tank and the other side is connected to a gas consuming system, a pressure sensor is disposed in the closed vessel in the other side. The pressure sensor can interlock with a relay switch connected between both the electrodes of the electrochemical cell to function to compensate for the consumption of gas.

15 Additional features and advantages of the present invention are described in, and will be apparent from, the following Detailed Description of the Invention and the figures.

BRIEF DESCRIPTION OF THE FIGURES

Fig. 1 is a schematic sectional view showing a usual example of a gas
20 regulator.

Fig. 2 is a schematic sectional view showing a pressure reducing device according to an embodiment of the present invention.

Fig. 3 is a graph showing a change of pressure of a high pressure vessel side of the pressure reducing device according to an embodiment of the present
25 invention.

Figs. 4A and 4B are structural views of polyhydroxylated fullerene showing one example of a fullerene derivative usable for the present invention pursuant to an embodiment.

Figs. 5A and 5B are schematic views showing examples of fullerene
30 derivatives pursuant to an embodiment.

Figs. 6A to 6M are schematic views showing various examples of a carbon cluster as a nucleus in a proton conductor pursuant to an embodiment.

Figs. 7A to 7D are schematic views respectively showing other examples of the carbon cluster (partial fullerene structure) pursuant to an embodiment.

5 Figs. 8A to 8G are schematic views respectively showing other examples (diamond structure) of the carbon cluster pursuant to an embodiment.

Figs. 9A to 9H are schematic views respectively showing still other examples (clusters are bonded together) of the carbon cluster pursuant to an embodiment.

10 Figs. 10A and 10B show a carbon nanotube as the nucleus of the proton conductor, and Fig. 10C is a schematic view showing carbon fibers pursuant to an embodiment.

Fig. 11 is a schematic sectional view showing an electrochemical device according to the present invention pursuant to an embodiment.

15 Fig. 12 is a schematic sectional view showing a gas storage device according to the present invention pursuant to an embodiment.

Fig. 13 is a schematic sectional view of outlet and inlet pressure detecting means connected to the gas storage device according to the present invention pursuant to an embodiment.

20 Fig. 14 is a schematic sectional view showing the gas storage device according to the present invention and a gas storage assist system connected thereto pursuant to an embodiment.

Fig. 15 is a schematic sectional view of another example of the gas storage device according to the present invention pursuant to an embodiment.

25 Fig. 16 is a schematic sectional view of a still another example of the gas storage device according to the present invention pursuant to an embodiment.

Fig. 17 is a schematic sectional view showing a gas storage device in which an electrochemical cell is formed in a multistage structure pursuant to an embodiment.

Fig. 18 is a schematic sectional view of another example of the gas storage device in which the electrochemical cell is formed in a multistage structure pursuant to an embodiment.

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DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a pressure reducing device, an electrochemical device, a pressure reducing and pressurizing device, a gas storage device, a gas storage assist system, and a method for driving these devices.

Various embodiments of the present invention will be described by referring
10 to the drawings.

A pressure reducing device according to the present invention includes as shown in Fig. 2, an electrochemical cell 4 as a partition wall, having first and second catalytic electrodes 1 and 2 respectively forming first and second electrodes on which catalysts such as platinum are carried and a proton conductor 3
15 sandwiched in between the catalytic electrodes 1 and 2, and a high pressure vessel 5 and a low pressure vessel 6 disposed at both the sides of the electrochemical cell 4. A vacuum pump 8 is connected to the high pressure vessel 5 and the low pressure vessel 6 through a vacuum line 7. Further, an H₂ reservoir 9 and a gas flow meter 10 are connected to the high pressure vessel 5 and the low pressure vessel 6. To
20 each of the vessels 5 and 6, lead introducing terminals 11 and 12 are connected. To the end of the gas flow meter 10, a power generation device using hydrogen gas as fuel, whose illustration is omitted, is connected.

Firstly, valves 13, 14 and 17 were closed to open valves 15 and 16 and obtain a vacuum in the high pressure vessel 5 and the low pressure vessel 6 by
25 using the vacuum pump 8. Then, the valves 15 and 16 were closed to open the valves 13 and 14 and introduce the hydrogen gas of 10 atmospheric pressure to each of the vessels 5 and 6 by the H₂ reservoir 9. After that, the valves 13 and 14 were closed. Then, the valve 17 was opened to have only the low pressure vessel 6 of 1 atm.

At this time, when a voltage difference between the lead introducing terminal 11 and 12 connected to both the ends of the electrochemical cell 4 was measured, the voltage difference was about 100 mV.

Then, both the electrodes 1 and 2 of the electrochemical cell 4 were short-circuited to measure the change of pressure of the high pressure vessel 5. Fig. 3 is a graph showing the change of pressure of the high pressure vessel 5 with the lapse of time. As shown in Fig. 3, it was recognized that the pressure in the high pressure vessel 5 decreased with the lapse of time t and the short-circuit between both the electrodes 1 and 2 by a relay functioned.

The proton conductor 3 is desirably composed of a derivative formed in such a way that a material made of at least one kind, such as fullerene molecules, a cluster having carbons as a main component and a tubular or linear carbon structural body or the like, is prepared as a main component and a proton dissociation group is introduced to carbon atoms forming the material. Additional embodiments described below are the same as the above.

Here, the proton dissociation group means a functional group in which protons can be separated in accordance with an electrolytic dissociation. The dissociation of the protons means that the protons are separated from the functional group in accordance with the electrolytic dissociation.

The fullerene molecules as a nucleus of an object to which the proton dissociation group is introduced may be any spherical shell type cluster molecules C_m where m indicates a natural number in which C_m may form a spherical shell structure. without a special limitation. In an embodiment, a single material of fullerene molecules selected from C_{36} , C_{60} , C_{70} , C_{76} , C_{78} , C_{80} , C_{82} , C_{84} , C_{86} , C_{88} , C_{90} , C_{92} , C_{94} , C_{96} , or the mixture of two kinds or more materials thereof are preferably employed.

The fullerene molecules were found in the mass spectrometry spectrum of a cluster beam of carbons by a laser ablation in 1985 (Kroto, H.W.; Heath, J. R.; O'Brien, S.C.; Curl, R.F.; Smalley, R.E. Nature 1985. 318, 162.). A producing method was established about five years later. In 1990, a producing method of a

carbon electrode by an arc discharge method was found in 1990. Then, fullerene has been paid attention to as a carbon semiconductor material or the like since then.

As shown in Figs. 4A and 4B, as Fullerenol having a structure formed by adding a plurality of hydroxyl groups to fullerene molecules, a synthesized example
5 was firstly reported by Chiang et al. in 1992 (Chiang, L.Y.; Swirczewski, J.W.; Hsu, C.S.; Chowdhury, S.K.; Cameron, S.; Creegan, K., J. Chem. Soc, Chem. Commun. 1992, 1791).

When the inventors of the present invention used the fullerenol as an aggregate as shown in Fig. 5A to generate a mutual interaction between hydroxyl
10 groups of the fullerenol molecules (in the drawing, \circ represents a fullerene molecule) which come into close contact with each other, they could initially recognize that the aggregate exhibited high proton conductive characteristics as a macro aggregate, that is, the aggregate exhibited the dissociation characteristics of H^+ from the phenolic hydroxyl groups of the fullerenol molecules.

According to the present invention, the aggregate of fullerene having, for instance, a plurality of $-OSO_3H$ groups except fullerenol can be used as the ion
15 conductor. Polyhydroxylated fullerene as shown in Fig. 5B in which an OH group is replaced by an OSO_3H group, that is, hydrogensulfate esterified fullerenol was also reported by Chiang et al. in 1994 (Chiang, L.Y.; Wang, L.Y.; Swirczewski, J.W.; Soled, S.; Cameron, S., J. Org. Cem. 1994, 59, 3960). In the hydrogensulfate
20 esterified fullerene, one molecule may include only OSO_3H groups or may include a plurality OSO_3H groups and hydroxyl groups, respectively.

When a lot of the above-described fullerenols and hydrogensulfate esterified fullerenols are aggregated, a proton conductivity shown by them as a bulk is
25 directly related to the movement of protons derived from a large quantity of hydroxyl groups or OSO_3H groups originally included in the molecules. Accordingly, the fullerenols and the hydrogensulfate esterified fullerenols can be continuously employed even under an atmosphere of low humidity.

The fullerene constituting the base of these molecules especially has
30 electrophilic characteristics, which is considered to greatly contribute to the acceleration of the electrolytic dissociation of hydrogen ions not only in OSO_3H

groups high in acidity, but also in hydroxyl groups and exhibits an excellent proton conductivity. Since a relatively large quantity of hydroxyl groups and OSO_3H groups can be introduced to one fullerene molecule, the density of the proton conductor related to conduction per unit volume becomes very high. Thus, a substantial conductivity is realized.

Most of the fullerenol and the hydrogensulfate esterified fullerenol are composed of fullerene carbon atoms, they are light and hardly deteriorated and include effectively no contaminated material. The production cost of fullerene is being rapidly lowered. The fullerene is considered to be a substantially ideal carbon material more than any other materials from the viewpoints of resources, environment and economy.

Further, the proton dissociation group does not need to be limited to the above-described hydroxyl group or the OSO_3H group.

That is, the proton dissociation group is represented by a formula $-\text{XH}$. X may be an arbitrary atom or an atomic group having a bivalent bond. Further, this group is represented by a formula $-\text{OH}$ or $-\text{YOH}$. Y may be an arbitrary atom or an atomic group having a bivalent bond.

Specifically, as the proton dissociation group, any one of $-\text{COOH}$, $-\text{SO}_3\text{H}$, $-\text{OPO}(\text{OH})_2$, and $-\text{C}_6\text{H}_4-\text{SO}_3\text{H}$ in addition to $-\text{OH}$ and $-\text{OSO}_3\text{H}$ is preferable.

To synthesize fullerenol usable in the present invention, for instance, well-known processes such as acidification or hydrolysis are suitably combined and applied to fullerene powder, so that desired groups can be introduced to carbon atoms forming the fullerene molecules.

Then, an obtained fullerene derivative is formed in the configuration of a film by an application or a deposition method to be used for the proton conductor 3 of the electrochemical cell 4.

The proton conductor 3 may be substantially composed of only the fullerene derivative or the fullerene derivative may be bonded by a binding agent.

When the proton conductor 3 is substantially composed of only the fullerene derivative, a film shaped proton conductor 3 formed by molding the fullerene derivative under pressure may be used. When the fullerene derivative bonded by

the binding agent are used as the proton conductor 3, the proton conductor with an adequate strength can be formed by the binding agent.

As polymer materials usable as the binding agent, one kind or two or more kinds of polymers having well-known film forming characteristics are employed.

5 The proton conductor having such a structure can exhibit the same proton conductivity as that of the proton conductor composed of only the fullerene derivative.

Further, the film forming characteristics resulting from the polymer materials are given to the proton conductor differently from the proton conductor
10 made of only the fullerene derivative. Thus, the proton conductor formed by bonding the fullerene derivative using the binding agent can be used as a flexible proton conductor 3 higher in its strength than a compression-molded product of the powder of the fullerene derivative and having a gas permeation preventing function. A proton conductive thin film used at this time has the thickness of about 300 μm
15 or smaller.

As the polymer materials, any of materials that do not hinder the conductivity of protons (due to a reaction with the fullerene derivative) as much as possible and have film forming characteristics may be used without a special limitation. Ordinarily, a material having no electronic conductivity and having a
20 good stability is used. As specific examples, polyfluoroethylene, polyvinylidene fluoride, polyvinyl alcohol, and the like may be exemplified. These materials are preferable polymer materials from reasons described below.

Firstly, since polytetrafluoroethylene can more easily form a thin film having higher strength with a smaller amount of mixing than other polymer
25 materials, the polytetrafluoroethylene is preferable. In this case, the amount of mixing is about 3 wt% or less and preferably an amount as small as about 0.5 to about 1.5 wt%. The thickness of the thin film can be ordinarily reduced to about 100 μm to about 1 μm .

Polyvinylidene fluoride or polyvinyl alcohol is preferable, because the
30 proton conductive thin film having the excellent gas permeation preventing

function can be obtained. In this case, the amount of mixing is preferably located within a range of 5 to 15 wt%.

When each of the amount of mixing of polyfluoroethylene, polyvinylidene fluoride or polyvinyl alcohol is lower than the lower limit value of the above-described range, an adverse effect may be possibly given to a film formation.

In order to obtain the thin film of the proton conductor formed by bonding the fullerene derivatives respectively by the binding agent, a well-known film forming method such as a pressure molding method or an extrusion molding method may be employed.

In the device according to the present invention, the electrodes 1 and 2 and the fullerene derivative as the proton conductor 3 are preferably formed in flexible sheet shapes having a physically adequate strength in view of treatment and compactness.

Since the electrochemical cell 4 can effectively function in atmospheric air, even when temperature or humidity during an operation is not adjusted, the pressure of the hydrogen gas can be efficiently reduced.

The fullerene derivative formed by introducing the proton dissociation group to the carbon atoms forming fullerene molecules such as fullerenols is used as a material for forming the proton conductor 3. Thus, the electrochemical cell 4 can function in the atmospheric air under a state of low humidity even when there is no humidifier, differently from a case that Nafion as an H_3O^+ ion conductor is used.

That is, since the pressure of the hydrogen gas can be reduced in the atmospheric air under the state of low humidity, an initial operation can be accelerated upon reducing the pressure of hydrogen without requiring a time until a steady operation. For instance, the humidifier may be provided to similarly reduce the pressure of the hydrogen gas under the presence of water. However, the present invention does not essentially require the above-described conditions.

When Nafion as the H_3O^+ ion conductor is used, hydrogen is compressed and water is also generated, so that a dehumidifier is necessary. As compared therewith, in this embodiment of the present invention, even when the dehumidifier is not provided, the pressure of the hydrogen gas can be reduced.

Further, even when the humidifier is not provided, an electrochemical pressure reducing operation can be efficiently realized. Thus, the content of water of the hydrogen gas whose pressure is reduced is small. Accordingly, a dehumidifying process as a post-process can be made unnecessary.

5 Therefore, the electrochemical cell 4 can efficiently reduce the pressure of the hydrogen gas. The device according to the present invention is more compact and highly generalized.

 In the present invention, as the proton conductor, for instance, a cluster derivative, can be used in place of the fullerene derivative, which is obtained in
10 such a way that a cluster made of carbon powder is obtained by an arc discharge method of a carbon electrode, the carbon powder is acidified and a proton (H^+) dissociation group is introduced to the carbon powder.

 Here, the cluster ordinarily means an aggregate formed by bonding or aggregating together several to several hundred atoms. The aggregate enables a
15 proton conductivity to be improved, holds chemical characteristics to have adequate film strength and is liable to easily form a layer. This cluster indicates the aggregate that includes carbons as main components and is formed by bonding several to several hundred carbon atoms irrespective of kinds of carbon to carbon bonds. However, the cluster is not necessarily composed of only carbons of 100 %
20 and other atoms may be mixed therein. The aggregate that many carbons occupy including the above-described case is called a carbon cluster.

 Since the above-described proton conductor includes, as a main component, a material obtained by introducing the proton dissociation group to the carbon cluster as a nucleus, the proton is easily dissociated under a dry state. Thus, effects
25 similar to those of the above-described proton conductor as well as the proton conductivity can be realized. Since many kinds of carbonaceous materials as described below are included in the category of the above-described carbon cluster, a range of selection of the carbonaceous material is effectively wide.

 In this case, the carbon cluster is used as the nucleus, because a large
30 quantity of proton dissociation groups needs to be introduced to obtain good proton conductivity and the above-described thing can be realized by the carbon cluster.

Thus, the acidity of a solid proton conductor is extremely high. However, the carbon cluster is hardly oxide deteriorated differently from other ordinary carbonaceous materials, excellent in its durability and component atoms are tightly bonded together. Accordingly, even when the acidity is high, the bonds between
5 the atoms do not collapse, that is, the carbon cluster is hardly chemically changed and can maintain a film structure.

The proton conductor having such a structure can also exhibit the high proton conductivity even under a dry state. As shown Figs. 6 to 9, there are various kinds of carbon clusters. As the materials of the proton conductor, a selection range
10 is widened.

Firstly, various kinds of carbon clusters are shown in Figs. 6A to 6M, which include many carbon atoms aggregated and having spherical or long spherical structures or closed surface structures similar thereto. In this case, molecular fullerene is shown together therewith. On the other hand, various kinds of
15 examples of carbon clusters are shown in Figs. 7A to 7D, in which the spherical structures are partly deficient. The carbon clusters shown herein are characterized in that open ends are provided in the structures. Most of the structures are produced as by-products in the production processes of fullerene by an arc discharge method. When most of the carbon atoms of the carbon cluster are bonded in SP³, various
20 kinds of clusters having the structures of diamond are produced as shown in Figs. 8A to 8G. In Figs. 7C and 7D, painted-out parts in black show a five-membered ring or a seven-membered ring.

The clusters in which the carbon atoms are substantially bonded in SP² have plane structures of graphite or all or a part of the structures of fullerene or a
25 nanotube. Since the clusters having the graphite structures of them substantially have an electronic conductivity therein, these clusters are not preferable as the nucleus of the proton conductor.

On the other hand, since the clusters having the SP² bonds of fullerene or the nanotube partly include a factor of the SP³ bonds, most of them do not have the
30 electronic conductivity, so that these clusters having the SP² bonds are preferable as the nucleus of the proton conductor.

Figs. 9A to 9G show various kinds of cases that clusters are bonded together. Such structures may be applied to the present invention. In Figs. 9A and 9B, ~ indicates a bond chain such as $(CH_2)_n$, $(CF_2)_n$ or the like. Further, in Figs. 9E to 9G, painted-out parts in black represent five-membered rings or seven-membered rings.

In the present invention, the above-described proton dissociation group needs to be introduced to carbon atoms forming the carbon cluster. As means for introducing the proton dissociation group, a below-described producing method is preferable.

That is, the carbon cluster made of carbon powder is firstly produced by the arc discharge of the carbon electrode. Subsequently, the carbon cluster is acidified, or a process such as a hydrolysis is further performed or a sulfonation is further performed or phosphate esterification is suitably formed. Thus, a carbon cluster derivative as a desired product can be easily obtained. In the above-described acidifying process, sulfuric acid or the like is used.

The carbon cluster can be directly formed in the shape of a film, pellets or the like under pressure without a binder. In the present invention, the carbon cluster as the nucleus preferably has the length of a major axis of 100 nm or shorter, especially preferably 100 Å or lower and the number of groups introduced thereto is desirably 2 or more.

As the carbon cluster, a cage type structure of fullerene or the like or a structure having open ends in at least a part thereof is preferable. Fullerene having such a defective structure has the reactivity of fullerene. At the same time, the defective part, that is, the opening part additionally has a higher reactivity. Accordingly, acid (proton) dissociation substituent groups are promoted to be introduced by the acidifying process to obtain a higher substituent introduction rate and a high proton conductivity. Further, a larger quantity of fullerene with the above-described structure can be synthesized than ordinary fullerene and produced at an extremely low cost.

On the other hand, as the nucleus of the proton conductor of the present invention, the tubular or the linear carbon structure is preferably used. As the

tubular carbon structure, a tube shape, for instance, a carbon nanotube is preferably used. As the linear carbon structure, a fiber type shape, for instance, a carbon fiber is preferably used.

5 The carbon nanotube or the carbon fiber is apt to structurally easily discharge electrons and can greatly increase its surface area. Thus, the carbon nanotube or the carbon fiber can more improve a proton propagation efficiency.

Here, the preferably usable carbon nanotube or the carbon fiber can be produced by the arc discharge method or a chemical gas phase deposition method (a thermal CVD method).

10 In the arc discharge method, a metal catalyst such as FeS; Ni, Co, or the like is used and a carbon nanotube or carbon fiber material is synthesized under an atmosphere of He, for instance, an atmosphere of 150 Torr by using an arc discharge chamber. The carbon nanotube material is stuck to the inner surface of the chamber in the shape of a cloth in accordance with an arc discharge. Thus, for
15 instance, the carbon nanotube can be obtained. In this case, when the catalyst coexists, the carbon nanotube having a small diameter can be obtained. When the arc discharge is carried out under the condition of having no catalyst, the thick carbon nanotube having many layers can be obtained.

As described above, the carbon nanotube can be produced by, for instance,
20 carrying out the arc discharge under the condition of having no catalyst. A multi-layer carbon nanotube 101 shown in Fig. 10A and a multi-layer carbon nanotube 201 with a graphene structure (a cylindrical structure) shown in Fig. 10B is known as a high quality carbon nanotube having no defect and having a very high performance as an electron discharging material.

25 The proton dissociation group can be introduced to the carbon nanotube obtained as described above by the arc discharge method in the same processes as mentioned above. Thus, a proton conductor excellent in its proton conductivity even under a dry state can be obtained.

The chemical gas phase deposition method is a method for synthesizing the
30 carbon nanotube or the carbon fiber by allowing fine particles of transition metals to react with hydrocarbons or CO of acetylene, benzene, ethylene, and the like. A

transition metal base or a coat base is allowed to react with hydrocarbon gas or CO gas to accumulate the carbon nanotube or the carbon fiber 301 on the base 300 as shown in Fig. 10C.

For instance, an Ni base 300 is disposed in an alumina tube heated at about 700°C and allowed to react with toluene/H₂ gas (for instance, 100 sccm) so that the carbon fiber 301 having the structure as shown in Fig. 10C can be synthesized.

Here, the aspect ratio of the carbon nanotube preferably ranges from about 1 : 1000 to about 1 : 10. Further, the aspect ratio of the carbon fiber preferably ranges from about 1 : 5000 to about 1 : 10. The diameter of the tubular or linear carbon structure is preferably located within a range of about 0.001 to about 0.5 μm. The length is preferably about 1 to about 5 μm.

In the device according to the present invention, only the single electrochemical cell serving as a pressure partition wall may be disposed. However, a plurality of electrochemical cells may be arranged in parallel in a gas flowing direction and may have a multistage structure. Especially, when the difference of pressure of the vessels disposed at both the sides of the electrochemical cell is large, several electrochemical cells need to be used.

The present invention concerns an electrochemical device. The electrochemical device includes a pressure reducing part including an electrochemical cell having a first electrode for decomposing hydrogen gas into protons, a second electrode for converting the protons produced in the first electrode into the hydrogen gas again and a proton conductor sandwiched in between both the electrodes and a high pressure vessel disposed in the first electrode side of the electrochemical cell to accommodate a gaseous material including the hydrogen gas; the electrochemical cell functioning to reduce pressure in the high pressure vessel; and a gas consuming part including a hydrogen gas storage part disposed in contact with the second electrode side in the pressure reducing part, a third electrode disposed in contact with the hydrogen storage part for decomposing the hydrogen gas supplied from the hydrogen gas storage part into protons; a fourth electrode for converting the protons generated in the third electrode into water, and a proton conductor sandwiched in between both the

electrodes, the protons being converted into water in the fourth electrode to take out electrochemical energy between the third electrode and the fourth electrode.

As a method for driving the electrochemical device according to the present invention, for instance, when the pressure reducing part is driven, the
5 electrochemical cell functions to reduce pressure in the high pressure vessel and the hydrogen gas storage part is disposed in contact with the second electrode side in the pressure reducing part. The gas consuming part including the third electrode for decomposing the hydrogen gas supplied from the hydrogen gas storage part into protons; the fourth electrode for converting the protons generated in the third
10 electrode into water, and the proton conductor sandwiched in between both the electrodes is desirably disposed in contact with the hydrogen gas storage part to convert the protons into water in the fourth electrode and take out the electrochemical energy between the third electrode and the fourth electrode.

In the electrochemical device according to the present invention, since a
15 mechanical movable part is not provided in the electrochemical device like the above-described gas pressure regulator according to the present invention, a compact, durable and silent device can be realized.

A specific structure of the electrochemical device according to the present invention is shown in Fig. 11.

20 As shown in Fig. 11, a pressure reducing part 18 includes an electrochemical cell 4 having a first electrode 1 for decomposing hydrogen gas into protons, a second electrode 2 for converting the protons produced in the first electrode 1 into the hydrogen gas again and a proton conductor 3 sandwiched in between both the electrodes 1 and 2, and a high pressure vessel 5 disposed in the
25 first electrode 1 side of the electrochemical cell 4 to accommodate a gaseous material including the hydrogen gas. The electrochemical cell 4 functions to reduce pressure in the high pressure vessel 5. A hydrogen gas storage part 19 is disposed in contact with the second electrode 2 side of the pressure reducing part 18. A gas consuming part 20 is disposed in contact with the hydrogen gas storage part 19 and
30 includes a third electrode 21 disposed in contact with the hydrogen storage part 19 for decomposing the hydrogen gas supplied from the hydrogen gas storage part 19

into protons, a fourth electrode 22 for converting the protons generated in the third electrode 21 into water, and a proton conductor 23 sandwiched in between both the electrodes 21 and 22. The protons can be converted into water in the fourth electrode 22 and electrochemical energy can be taken out between the third
5 electrode 21 and the fourth electrode 22 to serve as a fuel cell part. In the surface side of the fourth electrode 22 that does not come into contact with the proton conductor 23, O₂ or O₂ containing gas is supplied.

A pressure sensor 24 is disposed in the hydrogen gas storage part 19. The pressure sensor 24 serves to interlock with a relay switch 11a connected between
10 lead introducing terminals 11 and 12 connected between the first and second electrodes 1 and 2 of the electrochemical cell 4 to compensate for the consumption of gas.

The high pressure vessel 5 is connected to an H₂ supply tank 25 through a valve 25a. When pressure in the high pressure vessel 5 reaches a prescribed value
15 or smaller, the valve 25a is opened so that hydrogen gas can be supplied from the H₂ supply tank 25. The H₂ supply tank 25 may be filled with a hydrogen gas storing alloy, a hydrogen gas storing carbon material, metal halide, etc. As the hydrogen gas storing alloys, LaNi₆, CaNi₅, TiCo_{0.5}Mn_{0.5}, TiCo_{0.5}Fe_{0.5}, TiFe_{0.8}Ni_{0.15}V_{0.05}, etc. may be employed. As the hydrogen gas storing
20 materials, carbon materials, carbon nanotubes, carbon fibers, activated carbons, etc. may be employed. As the metal halides, NaAlH₄, LiAlH₄, etc. may be employed. The high pressure vessel 5 may be also filled with the hydrogen gas storing alloy, the hydrogen gas storing carbon material, the metal halide, and the like.

In this case, since the gas interrupting characteristics of the proton
25 conductors 3 and 23 must be high, the proton conductors 3 and 23 need to have characteristics in which ionized gas is permeated, however, gas itself is not permeated. To realize the above-described characteristics, the proton conductors 3 and 23 are desirably composed of a derivative formed in such a way that at least one kind of material selected from a group including fullerene molecules, a cluster
30 having carbons as a main component, and a tubular or linear carbon structure is

included as a main component, and a proton dissociation group is introduced to carbon atoms forming this material in the same manner as described above.

The present invention concerns a gas storage device including a gas inlet and outlet part for introducing or discharging gas; a gas storage part for storing gas;
5 an electrochemical cell disposed in the gas storage part and including a first electrode for decomposing the gas into ions, a second electrode for converting the ions generated in the first electrode into the gas again and an ion conductor sandwiched in between both the electrodes; and a pressure reducing and pressurizing part in which the gas is supplied to or discharged from the gas storage
10 part through the gas inlet and outlet part in accordance with the function of the electrochemical cell to decrease or increase pressure in the gas storage part.

As a method for driving the gas storage device according to the present invention, for instance, when the gas storage device is driven, the gas is desirably supplied to or discharged from the gas storage part through the gas inlet and outlet
15 part in accordance with the function of the electrochemical cell to decrease or increase pressure in the gas storage part.

In the gas storage device according to the present invention, since a mechanical movable part is not provided in the gas storage device like the above-described gas pressure regulator or the electrochemical device according to the
20 present invention, the compact and durable gas storage device can be realized.

A gas storage device 26 according to the present invention has a structure as shown in Fig. 12. A gas inlet and outlet part 27 provided in the gas storage device 26 has an opening for inputting and outputting gas and a micro space sufficient for temporarily holding gas under equal pressure.

25 Inlet and outlet pressure detecting means 28 is provided for detecting pressure in the micro space and is, for instance, a pressure sensor using a diaphragm. As one example of such a pressure sensor, for instance, a pressure sensor having a diaphragm 29, a closed space 30 in which a prescribed quantity of gas is sealed and a micro-switch 31 as shown in Fig. 13 is used.

30 One surface side of the diaphragm 29 has the same pressure as that of the gas inlet and outlet part 27. Thus, the diaphragm 29 is moved until the differential

pressure of the pressure of the closed space 30 and the pressure of the gas inlet and outlet part 27 is balanced to the resilient force of the diaphragm 29. When the pressure of the gas inlet and outlet part 27 reaches prescribed pressure, the micro-switch 31 is switched from ON (a connected state) to OFF (a disconnected state).

5 A pressure wall 32 is a pressure resistant wall for holding high pressure, for instance, 10 to 300 atmospheric pressure and has a gas moving hole as many openings with very small areas in the boundary of the gas inlet and outlet part 27 and the pressure wall 32. The form of the pressure wall 32 is not especially limited to a specific form, however, to uniformly distribute the pressure, a cylindrical form
10 or a spherical form is more preferable. Fig. 12 shows a sectional view taken along a plane including the center of a cylinder when the form of the pressure wall 32 is a cylindrical form.

 The gas moving hole holds a first electrode 1, an ion conductor 3 and a second electrode 2 against the pressure of a gas storage part 33, and at the same
15 time, can move gas from the gas storage part 33 to the gas inlet and outlet part 27. An electrochemical cell including the first electrode 1, the ion conductor 3 and the second electrode 2 is a pressure reducing and pressurizing part operating as independent parts and the entire part of the electrochemical cell is held in the gas storage part 33.

20 Lead lines 34 and 35 are electric conductors having their one ends respectively connected to the second electrode 2 and the first electrode 1. The other ends of the lead lines are connected to a second electrode terminal 38 and a first electrode terminal 39 while insulation from the pressure wall 32 is maintained. A connecting line 36 and a connecting line 37 connects respectively the contacts of
25 the second electrode terminal 38 and the first electrode terminal 39 and the micro-switch 31 together.

 The gas storage device 26 according to the present invention includes a gas storage assist system. The gas storage assist system desirably comprises a gas passage for supplying the gas to the gas inlet and outlet part 27 provided in the gas
30 storage device 26; a pressure detecting means for detecting gas pressure in the gas passage 41; a voltage detecting means for detecting voltage generated between the

first electrode 1 and the second electrode 2; a calculating means for calculating a control current signal on the basis of the gas pressure and the voltage; a current supply means for generating a control current; and a switching means for alternately switching a state that the control current is supplied between the first
5 electrode 1 and the second electrode 2 and a state that the voltage is detected until the voltage reaches a predetermined value.

The gas storage device 26 having the gas storage assist system 40 according to the present invention is shown in Fig. 14. A part shown by a broken line in Fig. 14 represents the gas storage device 26 and a part shown by a full line represents
10 the gas storage assist system 40.

The passage 41 has a structure connected to the opening part of the gas inlet and outlet part 27 provided in the gas storage device 26 so that gas does not leak. The gas is supplied to the passage 41 from a tank 47.

A pressure detecting mechanism 42 can detect the pressure value of the gas
15 in the passage 41, and, for instance, changes the displacement of a diaphragm to a resistance value to an analog pressure value of P1. The pressure detecting mechanism 42 is provided for the purpose of detecting the pressure of the gas inlet and outlet part 27 of the gas storage device 26, that is, the pressure applied to the second electrode 2 from the gas inlet and outlet part 27 side. Since the passage 41
20 is connected to the gas inlet and outlet part 27, they have the substantially same pressure. The pressure detecting mechanism 42 is provided in the vicinity of the passage 41, this purpose can be achieved.

A first terminal 48 and a second terminal 49 hold an electric contact with the first electrode terminal 39 and the second electrode terminal 38 of the gas
25 storage device 26.

A switching part 46 is switching means connected to the first terminal 48 and the second terminal 49 by electric conductive lines.

Contacts S0 and S1, and contacts S3 and S4 are turned on at the same time. When a switching signal C1 is changed, contacts S0 and S2, and contacts S3 and S5
30 are turned on at the same time. The switching signal C1 is transmitted from a calculating part 44. When switching members 43a and 44a of a switch are

connected to the contacts S1 and S4, a pressure voltage detecting part 43 detects voltage generated between the first electrode 1 and the second electrode 2. When the switching members 43a and 44a of the switch are connected to the contacts S2 and S5, prescribed current is supplied to the first terminal 48 and the second terminal 49 from a current supply part 45.

The direction and the quantity of the current are determined by a current control signal C2 and the values are calculated by the calculating part 44.

An operation upon discharging gas in the gas storage device 26 is carried out as described below in the same manner as that of the pressure reducing device according to the present invention.

Voltage corresponding to the pressure difference between the storage part 33 and the gas inlet and outlet part 27 is generated between the first electrode terminal 39 and the second electrode terminal 38 of the gas storage device 26 and guided to the respective contacts of the micro-switch 31 via the connecting line 36 and the connecting line 37. When the pressure of the gas inlet and outlet part 27 is lowered to a prescribed value or smaller, the contact of the micro-switch 31 is turned ON. Thus, current is supplied to the second electrode 2 and the first electrode 1 on the basis of the generated voltage and ions are supplied to the ion conductor 3. As a result, the pressure of gas in the gas storage part 33 is reduced and the pressure reduced gas is supplied to the gas inlet and outlet part 27. When the gas inlet and outlet part 27 is sufficiently filled with the gas, the contact of the micro-switch 31 is turned OFF to interrupt the current of the second electrode 2 and the first electrode 1. Consequently, the conduction of the ions is interrupted to stop the entry of the gas in the gas storage part 33 to the gas inlet and outlet part 27.

As a contact form of the micro-switch 31, when a switch of a type that hysteresis characteristics, namely, different pressure allows the switch to shift to each of states of ON/OFF is used, the ON/OFF operations of the switch can be slowly repeated within a prescribed range of pressure change. Thus, the life of the contact of the switch can be effectively lengthened.

Thus, since the gas inlet and outlet part 27 is filled with gas of prescribed pressure, the gas of the prescribed pressure can be taken out from an opening part.

In the processes of the operation, external electric power is not required, so that the gas storage device high in its reliability and easy in its maintenance can be provided.

Now, an operation of the gas storage device 26 upon storing gas will be
5 described by referring to the above-described Figs. 12 to 14.

When the gas is stored, the gas storage device 26 is connected to the gas storage assist system 40 to store the gas.

The connecting line 36 and the connecting line 37 of the gas storage device 26 are temporarily removed or one of the connecting lines is disconnected by a
10 switch which is provided halfway and is not illustrated. Then, the passage 41 is connected to the opening part of the gas inlet and outlet part 27, and the first terminal 48 and the second terminal 49 are connected to the first electrode terminal 39 and the second electrode terminal 38.

The switching part 46 is switched to a pressure detecting operation side by
15 the switching signal C1 and pressure voltage is detected by the pressure voltage detecting part 43. Here, pressure in the second electrode 2 is detected as an output P1 from the pressure detecting mechanism 42. Accordingly, the pressure of gas in the gas storage part 33 is obtained as P2 by substituting the obtained values for the above-mentioned formula (1).

20 When the pressure P2 is lower than the withstanding pressure of the pressure wall 32 of the gas storage part 33, even if the gas storage part is further filled with gas, the pressure wall 32 is not broken. Thus, the gas storage part can be further filled with the gas. To move the gas to the gas storage part 33, the switching part 46 may be switched by the switching signal C1 to supply current and
25 a prescribed current in an opposite direction to that of the current upon discharging the gas may be applied to the second electrode 2 and the first electrode 1.

When the intensity of the current more increases, an amount of movement of gas more increases, so that the gas storage part can be rapidly filled with the gas. However, when excessive current is supplied, the ion conductor 3 may be possibly
30 broken. Therefore, the current needs to be located within a limited range.

As the prescribed current, a constant current may be supplied throughout all period of filling of gas, or a quantity of current may be arbitrarily controlled in accordance with the progress of the filling of gas.

5 The switch of the switching part 46 is alternately switched to alternately fill the storage part 33 with gas and monitor the pressure of the storage part 33. Thus, the pressure of the gas in the storage part 33 can be raised until prescribed pressure is finally obtained.

Thus, while the pressure of the storage part 33 is monitored without providing the pressure sensor in the storage part 33, the storage part 33 can be safely filled with the gas. Accordingly, the structure of the storage part 33 can be effectively simplified. Further, in the gas storage assist system 40 side, since a part under a high pressure state does not exist, the gas storage assist system 40 itself can be made inexpensive and can be safely used in an ordinary home at the same time.

15 Fig. 15 shows an example in which other electrochemical cell is provided in the gas storage device 26 shown in Fig. 12. Since members designated by the same reference numerals as those shown in Fig. 12 are the same members having the same operational functions, the detailed description thereof is omitted.

A third electrode 21 is provided in contact with the opening part of a gas inlet and outlet part 27. A second proton conductor 23 is disposed between the third electrode 21 and a fourth electrode 22. A third terminal 50 is electrically connected to the third electrode 21. A fourth terminal 51 is connected to the fourth electrode 22. An arrow mark shown by 52 indicates that liquid material or gaseous material is supplied to the fourth electrode 22.

25 Now, an operation of the gas storage device shown in Fig. 15 will be described below.

When specific materials are supplied to the third electrode 21 and the fourth electrode 22, the gas storage device according to the present invention shown in Fig. 15 can serve as a fuel cell in accordance with the actions of the third electrode 21, the proton conductor 23 and the fourth electrode 22. Here, in accordance with the materials respectively supplied to electrode films, the third electrode 21 serves

as an anode or a cathode and the fourth electrode 22 serves as a cathode or an anode. For instance, when hydrogen gas is supplied to the third electrode 21 and air (oxygen containing gas) or oxygen gas is supplied to the fourth electrode 22, the third electrode 21 serves as the anode and the fourth electrode 22 serves as the cathode. Thus, negative voltage can be obtained from the third terminal 50 and positive voltage can be obtained from the fourth terminal 51.

The operation until the gas of prescribed pressure is obtained in the gas inlet and outlet part 27 is the same as described above.

When the positive voltage is applied to the fourth terminal 51 and the negative voltage is applied to the third terminal 50 and pure water or water vapor is supplied to the fourth electrode 22, the hydrogen gas can be obtained in the gas inlet and outlet part 27. An operation that the hydrogen gas in the gas inlet and outlet part 27 is pressurized to store the gas in the gas storage part 33 is the same as described above.

This device is a compact and portable device capable of producing gas such as hydrogen gas and generating power. Accordingly, the device is useful for using electric power in outdoors and for a power supply for emergency.

Fig. 16 shows a gas storage device 126 having a display part 53 for displaying the state of the gas storage device 26. The above-described state indicates, for instance, the pressure in the gas storage part 33, the filled state of the gas in the gas storage part 33, the remaining quantity of gas, or whether or not the electrochemical cell having the first electrode 1 and the second electrode 2 carrying catalysts for ionic bond or ionic dissociation normally functions, etc.

When the pressure of the gas inlet and outlet part 27 is understood from the formula of Nernst represented by the above-described formula (1), the pressure of the gas storage part 33 can be recognized. When the gas storage device 26 operates, the gas inlet and outlet part 27 is maintained to prescribed pressure in accordance with the operation of the pressure detecting means 28. Thus, the pressure of the gas storage part 33 can be grasped.

The pressure of the gas storage part 33 also shows the filled state of the gas in the gas storage part 33 at the same time. Since the reduction of pressure in the

gas storage part 33 means the decrease of the quantity of filled gas, the filled state or the remaining quantity of gas can be recognized thereby.

When the electrochemical cell normally operates while the device operates, the micro-switch 31 provided in the pressure detecting means 28 repeats ON/OFF
5 operations. Accordingly, when the operations are detected, it can be decided whether or not the operation of the electrochemical cell is normal.

The display part 53 is composed of, for instance, a voltmeter or a light emitting element such as an LED. A connecting line 54 is connected to the second electrode 2 and a connecting line 55 is connected to the first electrode 1. A
10 connecting switch 56 is connected on the way thereto. Only when the display part 53 is used, a push button 57 is pressed to connect a circuit. The display part 53 may be ordinarily disconnected from an electrode film.

When the display part 53 is the voltmeter, the pointer of the voltmeter swings in accordance with the ON/OFF operations of the micro-switch 31. At the
15 time of ON, since the first electrode 1 and the second electrode 2 are short-circuited, the pointer of the voltmeter points zero. At the time of OFF, voltage is generated, that is, voltage corresponding to a pressure difference is generated.

Although the internal resistance of the voltmeter is high, a little current is always continuously supplied between the electrodes. Thus, a very small quantity
20 of gas flows out from the gas storage part 33. Thus, when a display is not requested, the display part 53 is desirably disconnected from the circuit. The display part 53 may be visually recognizable detecting means such as the LED or a buzzer as means depending on an auditory sense. An operating point is arbitrarily set by adjusting the light emission start voltage of the LED and the pressure of the
25 gas storage part 33 by a resistance division, or setting the specification of winding of the buzzer.

Thus, the state of the gas storage device 26 can be displayed without requiring external electric power. A refilling time can be effectively estimated, the remaining quantity of gas can be effectively detected and the normal operation of
30 the gas storage device 26 can be conveniently recognized.

Fig. 17 shows an example that a plurality of electrochemical cells are arranged in the gas storage device 26 to form a multistage structure.

High pressure gas is supplied to a high pressure side 58. Gas to be used is taken out from a low pressure gas side 59. Electrochemical cells 60 to 65 are arranged in such a way that empty chambers 66 to 70 are respectively arranged between the electrochemical cells. Each of the electrochemical cells has a proton conductor sandwiched in between two gas diffusion electrodes. A surface of the gas diffusion electrode that comes into contact with the proton conductor carries a catalyst.

A method for controlling each electrode of each electrochemical cell is the same as that of the previously described embodiment, a detailed explanation thereof is omitted.

In accordance with the device, the differential pressure at both the sides of each electrochemical cell is set to a prescribed constant value to sequentially perform a pressure reducing operation, so that a pressure difference applied to the single body of each electrochemical cell can be reduced. For instance, when six electrochemical cells are provided, assuming that the differential pressure applied to one electrochemical cell is 20 atmospheric pressure and the differential pressure applied to the low pressure side 59 is one atmospheric pressure, the pressure of the high pressure side 58 may be 121 atmospheric pressure. Irrespective of the large pressure difference such as 120 atmospheric pressure, the pressure resisting force of the electrochemical cell may withstand 20 atmospheric pressure. Accordingly, the design of the device is advantageously simplified.

In the device shown in Fig. 17, the empty chambers are respectively provided between the electrochemical cells. However, when a function for detecting the pressure of the empty chambers is not necessary, such empty chambers are not necessarily required. Fig. 18 shows a schematic sectional view of a device in which empty chambers are not provided between electrochemical cells.

The basic structure of the electrochemical cells 71 to 76 is the same as that shown in Fig. 17. However, gas diffusion electrodes can be commonly used with gas diffusion electrodes of next stages. Accordingly, the number of the gas

diffusion electrodes is decreased and the empty chambers are not provided between the electrochemical cells.

Now, an operation of this device will be described below.

Supplied hydrogen gas is electrically dissociated to electrons and protons
5 due to the action of a catalyst 78 carried on the surface of a gas diffusion electrode
77. The electrically dissociated protons move throughout a proton conductor due to
the action of a proton conductor 79. The protons are bonded to the electrons due to
the action of a catalyst 81 carried on the surface of a gas diffusion electrode 80 to
become the hydrogen gas again. The hydrogen gas is diffused in the gas diffusion
10 electrode 80 having many pores through which the gas passes.

The hydrogen gas permeates the gas diffusion electrode 80 according to a
concentration distribution and is electrically dissociated to the protons and the
electrons again due to the action of a catalyst 82 carried on the other surface of the
gas diffusion electrode 80. The electrically dissociated protons move due to the
15 action of a proton conductor 83 to reach a gas diffusion electrode 84. The protons
are returned to the hydrogen gas again in the gas diffusion electrode 84 due to the
action of a catalyst 85 carried on the surface of the gas diffusion electrode 84.

The above-described processes are repeated to sequentially reduce pressure.
Here, voltage is detected between the gas diffusion electrode 80 and the gas
20 diffusion electrode 84 as described above. Accordingly, for instance, when both
the electrodes are conducted to each other in accordance with the generated voltage
to supply current to the gas diffusion electrode 80 and the gas diffusion electrode
84, the pressure difference between the gas diffusion electrode 80 and the gas
diffusion electrode 84 can be maintained to a prescribed value. The pressure
25 resistance of the gas diffusion electrodes and the proton conductors can be made
substantially equal.

In this embodiment, an example that the hydrogen gas is used as gas is
described. However, oxygen gas may be used. In this case, as the ion conductor,
zirconium oxide is preferably employed.

30 The present invention is not limited to the above-described embodiments
stated by referring to the drawings. It is apparent for a person with ordinary skill in

the art that various changes, substitutions or equivalence thereto may be made without departing the attached claims and the gist thereof.

According to the present invention, since the mechanical movable part is not provided in the device, the compact, durable and silent pressure reducing device,
5 the electrochemical device, the pressure reducing and pressurizing device, the gas storage device and the gas storage assist system and a method for driving these devices can be realized.

The present invention is employed to make the device itself compact and portable. Thus, for instance, the electrochemical device that can be carried by an
10 individual and can easily operate various devices driven by using gas such as hydrogen gas can be obtained.

It should be understood that various changes and modifications to the presently preferred embodiments described herein will be apparent to those skilled in the art. Such changes and modifications can be made without departing from the
15 spirit and scope of the present invention and without diminishing its intended advantages. It is therefore intended that such changes and modifications be covered by the appended claims.

ABSTRACT OF THE DISCLOSURE

A gas pressure regulator and applications thereof are provided. The gas pressure regulator includes an electrochemical cell having a first electrode for decomposing gas into ions, a second electrode for converting the ions generated in
5 the first electrode into the gas again and an ion conductor sandwiched in between both the electrodes and; and a high pressure vessel disposed in one side of the electrochemical cell. In this device, the gas is decomposed into the ions in the first electrode. The decomposed ions are allowed to pass through the ion conductor sandwiched in between the first electrode and the second electrode and conducted
10 to the second electrode side. The conducted ions are reconverted into the gas in the second electrode.

Marked-Up Version of Substitute Specification

DESCRIPTION
SPECIFICATION

TITLE OF THE INVENTION

5 ELECTROCHEMICAL DEVICE AND GAS STORAGE DEVICE

CROSS REFERENCES TO RELATED APPLICATIONS

The present application claims priority to Japanese Patent Document Nos.
P2002-009456 filed on January 18, 2002, and P2002-373798 filed December 25,
10 2002, the disclosures of which are herein incorporated by reference.

BACKGROUND OF THE INVENTION

~~Technical Field~~

The present invention relates to a pressure reducing device, an
15 electrochemical device, a pressure reducing and pressurizing device, a gas storage
device, a gas storage assist system, and a method for driving these devices.

~~This application claims a priority on the basis of Japanese Patent
Application No. 2002-009456 filed on January 18, 2002 and Japanese Patent
Application No. 2002-373798 filed on December 25, 2002, the entireties of which
20 are incorporated by reference herein.~~

~~Background Art~~

~~As means for~~To converting high pressure gas into low pressure gas, a
mechanical gas regulator has been hitherto widely employed. The usual gas
regulator has been a mechanical device as disclosed in, for instance, Japanese
25 Patent Application Laid-Open No. H04-244506.

Now, according to the contents described in the Japanese Patent Application
Laid-Open No. H04-244506, the usual gas regulator will be described below.

The usual gas regulator is formed as shown in Fig. 1. That is, on one end of
an inlet side of a main body case 86, an inlet pipe 87 is mounted. On the other end,
30 an outlet port 88 is formed. To an opening part 86a formed on the upper surface of
the main body case 86, a cover 89 is fixed. Between the main body case 86 and the
cover 89, the peripheral edges of a diaphragm 90 are fixed. The diaphragm 90 air-

tightly partitions an atmospheric pressure chamber 91 of the cover 89 side and a pressure reducing chamber 92 in the case 86.

In the center of the diaphragm 90, an operating rod 93 vertically passes. The diaphragm 90 is sandwiched in and fixed between a collar part 93a provided in the operating rod 93 and a nut 94 screwed to an upper end of the operating rod 93. 5 A spring 95 is interposed between the diaphragm 90 and the cover 89 to constantly urge the diaphragm. To the lower part of the operating rod 93, the operating end of an operating lever 96 is cross-linked so as to slide. The operating lever 96 is supported by the case 86 through a support shaft 97 so as to rotate. An operating 10 end of the operating lever 96 is engaged with a valve body 98 that is opposed to an end nozzle part 87a of the inlet pipe 87 through an operating pin 99. In the cover 89, a vent hole 89a communicating with an atmospheric side is formed.

In the usual gas regulator constructed as described above, when an amount of gas consumed in a combustion device (~~an illustration is omitted, not shown~~) is 15 reduced to raise pressure in the pressure reducing chamber 92, the diaphragm 90 overcomes the urging force of the spring 95 to be displaced to the atmospheric pressure chamber 91 side, raise the operating rod 93 and rotate the operating lever 96 counterclockwise on the support shaft 97. The valve body 98 is allowed to come near to the nozzle part 87a. Thus, an amount of inlet of gas is decreased to lower 20 gas pressure in the pressure reducing chamber 92. In such a way, the gas pressure in the pressure reducing chamber 92 is maintained to a substantially constant value correspondingly to the urging force of the spring 95.

Accordingly, when high pressure gas (a gaseous material) is supplied from the inlet pipe 87 side, the gas of prescribed low pressure can be obtained in the 25 outlet port 88 side.

The usual gas regulator according to the above-described mechanical system has a large form in structural point of view. Further, since the above-described gas regulator has movable parts, an abrasion due to a friction is generated so that the life of a machine is shortened. Further, noise is undesirably generated 30 during an operation.

Further, the usual gas regulator merely intends to reduce the pressure of gas and is only provided with a pressure reducing mechanism. Thus, a pressurizing mechanism needs to be provided separately from the pressure reducing mechanism in order to apply pressure.

5

~~Disclosure of the Invention~~

SUMMARY OF THE INVENTION

The present invention relates to a pressure reducing device, an electrochemical device, a pressure reducing and pressurizing device, a gas storage device, a gas storage assist system, and a method for driving these devices.

~~It is an object of the present invention to provide~~ In an embodiment, the present invention ~~provides~~ a new pressure reducing device, an electrochemical device, a pressure reducing and pressurizing device, a gas storage device and a gas storage assist system, and a method for driving these devices that can solve problems ~~of the usually typically~~ associated with the conventional and proposed device for converting high pressure gas to low pressure gas as described above.

~~It is another object of the present invention to provide~~ In another embodiment, the present invention ~~provides~~ a compact, durable and silent pressure reducing device, an electrochemical device, a pressure reducing and pressurizing device, a gas storage device and a gas storage assist system, and a method for driving these devices.

The present invention concerns in an embodiment a gas pressure regulator ~~comprising including~~ an electrochemical cell including a first electrode for decomposing gas into ions, a second electrode for converting the ions generated in the first electrode into the gas again, and an ion conductor sandwiched in between both the electrodes; and a high pressure vessel disposed in one side of the electrochemical cell.

The present invention concerns in an embodiment a gas pressure regulating method ~~comprising including~~ a decomposing step of decomposing gas into ions in a first electrode; a conducting step of conducting the decomposed ions to a second electrode side through an ion conductor sandwiched in between the first electrode

and the second electrode; and a converting step of converting the conducted ions to the gas again in the second electrode.

5 In the gas pressure regulator and the gas pressure regulating method according to an embodiment of the present invention, since the decomposing step, the conducting step and the converting step are included and a mechanical movable part is not provided in the device, a compact, durable and virtually silent gas pressure regulator can be realized.

10 Here, when the gas pressure regulator according to an embodiment of the present invention is driven, for instance, the electrochemical cell can function to reduce pressure in the high pressure vessel.

The electrochemical cell functions to reduce or increase the pressure in the high pressure vessel, so that the gas pressure regulator according to the present invention can operate as a pressure reducing and pressurizing device.

15 In these cases, since a mechanical movable part is not provided in the gas pressure regulator according an embodiment of to the present invention, a compact, durable and silent device can be obtained. According to an embodiment of the present invention, since one device is formed so as to have a pressure reducing mechanism and a pressure applying mechanism, a more compact device than a usual gas regulator can be realized.

20 In the present invention, gas is desirably in a state of gas under ordinary temperature and ordinary pressure. Specifically, the gas is desirably hydrogen gas, ~~or~~ oxygen gas or the like according to an embodiment.

25 The ion conductor is preferably a film made of an electrolyte material capable of permeating ionized gas. Further, the first electrode and the second electrode are preferably electrode films on which a catalyst such as platinum capable of ionic equilibrium of gas is carried in an embodiment.

30 In an embodiment, ~~T~~the electrode preferably has a heat resistance and a large surface area as much as possible. Each electrode can preferably come into tight contact with the ion conductor over an entire surface through the catalyst carried on a surface. The electrode preferably has flexibility to some degree so as

to come into tight contact with the ion conductor. Further, the electrode is preferably an activated electrode.

Accordingly, the first electrode and the second electrode are preferably porous or mesh shaped in an embodiment. For instance, the first electrode and the
5 second electrode can be formed in such a way that carbon fibers or porous carbons are formed in a sheet shape and an active catalyst is carried on a side which comes into tight or intimate contact with the ion conductor made of the sheet shaped electrode material. To such a sheet shaped electrode material, a net shaped core material formed by braiding metal wires, as a core material, may be inserted or
10 stuck. The metallic core material is inserted or stuck to the electrode so that the electric conductivity of the electrode itself can be improved and a uniform current distribution over an entire surface can be expected.

The catalyst is desired to be fine particles of, for instance, platinum, ruthenium oxide, iridium oxide, ~~etc~~ and the like in an embodiment. Any other
15 suitable electrode materials such as silver by which a reaction as a purpose of the present invention proceeds may be employed.

The catalyst may be carried on the electrode by an ordinary method. For instance, a method may be used that a catalytic material or its precursor is carried on the surface of carbon powder, subjected to a process such as heating to form
20 catalytic particles and the catalytic particles are baked together with a fluoro-resin on the surface of the electrode. Further, an electrode body on which the catalytic material is not carried is previously formed. Then, a precursor of the catalytic material, for instance, the mixed aqueous solution of platinic chloride and ruthenium chloride or butyl alcohol solution is applied to the surface of the
25 electrode as application liquid and sintered in a reducing atmosphere including hydrogen at about 200°C to about 350°C. Thus, an alloy of platinum and ruthenium can be formed on the surface of the electrode pursuant to an embodiment.

The device according to an embodiment of the present invention has
30 preferably a low pressure vessel in the other side of the electrochemical vessel. The electrochemical cell preferably serves as a gas partition. ~~Means for regulating~~ The

pressure is regulated by controlling a potential between both the electrodes is preferably provided when a pressure difference is generated at both the sides of the electrochemical cell. Further, an electromotive force generated from the pressure difference is preferably short-circuited by a relay, ~~etc-or~~ the like or pressure is preferably regulated by a variable resistor.

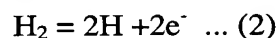
Ordinarily, when the pressure difference is generated at both the sides of the electrochemical cell, the electromotive force is generated from the pressure difference. This is known as the formula of Nernst including the term of pressure shown in a below-described formula:-

10
$$E = E_0 + (RT/2F) \ln(P1/P2) \dots (1)$$

In the formula (1), E_0 represents an ionized potential of gas, R represents a gas constant, T represents a temperature, F represents a Faraday constant, and P1 and P2 represent gas pressure.

Essentially, when the gas pressure is the same at both the sides of the electrochemical cell as the partition wall, a potential difference is not generated. However, when gas pressure in one side is raised, the electromotive force due to the term of $\ln(P1/P2)$ in the formula (1) is generated.

For instance, when the gas is hydrogen gas, equilibrium as shown by a below-described formula (2) exists on the catalyst such as platinum carried on the electrode.



When the pressure rises, this electrochemical equilibrium shifts to mitigate a stress. This reaction equilibrium causes a volume to be changed, which has a very important meaning. That is, when the pressure rises, the equilibrium shifts rightward so as to mitigate it. Thus, many electrons flow into the electrode to raise the potential. At the same time, many protons (H^+) are injected to the ion conductor in the high pressure vessel side so that the protons are apt to be diffused to the low pressure vessel side.

When the protons diffused to the low pressure vessel side are not recombined to the electrons, the protons cannot return to the hydrogen gas. Accordingly, when an electrical short-circuit in which the potential difference

between both the electrodes is constant is generated, the protons are recombined to the electrons in the low pressure vessel side. Thus, apparently, the hydrogen gas flows to the low pressure vessel side.

5 In this process, the gas interrupting characteristics of the ion conductor is required. As described below, for instance, when the hydrogen gas is used as the gas, a proton conductor including fullerene or the like as a base is useful for the ion conductor.

Basically, since only ions of specific gas can pass through the ion conductor, the electrochemical cell also has a function as a gas refining filter.
10 Accordingly, when the hydrogen gas is used as the gas, the electrochemical cell is most suitable as a regulator for supplying the hydrogen gas to an electrochemical device such as a fuel cell under prescribed pressure.

As described above, the essence of the present invention resides in the formula of Nernst depending on pressure, that is, the above-described formula (1).
15 When the pressure difference is generated between both the electrodes, the potential of both the electrodes can be short-circuited by a relay, ~~etc-or the like~~, or the potential of both the electrodes can be controlled by a variable resistor to regulate the pressure.

Both the sides of the electrochemical cell serving as the gas partition wall
20 have closed vessels. When one side serves as a high pressure gas tank and the other side is connected to a gas consuming system, a pressure sensor is disposed in the closed vessel in the other side. The pressure sensor can interlock with a relay switch connected between both the electrodes of the electrochemical cell to function to compensate for the consumption of gas.

25 ~~Still other objects of the present invention and specific advantages obtained by the present invention will become more apparent from the description of embodiments explained below by referring to the drawings.~~

Additional features and advantages of the present invention are described in, and will be apparent from, the following Detailed Description of the Invention and
30 the figures.

BRIEF DESCRIPTION OF THE DRAWINGSFIGURES

Fig. 1 is a schematic sectional view showing a usual example of a gas regulator.

Fig. 2 is a schematic sectional view showing a pressure reducing device
5 according to an embodiment of the present invention.

Fig. 3 is a graph showing a change of pressure of a high pressure vessel side of the pressure reducing device according to an embodiment of the present invention.

Figs. 4A and 4B are structural views of polyhydroxylated fullerene showing
10 one example of a fullerene derivative usable for the present invention pursuant to an embodiment.

Figs. 5A and 5B are schematic views showing examples of fullerene derivatives pursuant to an embodiment.

Figs. 6A to 6M are schematic views showing various examples of a carbon
15 cluster as a nucleus in a proton conductor pursuant to an embodiment.

Figs. 7A to 7D are schematic views respectively showing other examples of the carbon cluster (partial fullerene structure) pursuant to an embodiment.

Figs. 8A to 8G are schematic views respectively showing other examples (diamond structure) of the carbon cluster pursuant to an embodiment.

20 Figs. 9A to 9H are schematic views respectively showing still other examples (clusters are bonded together) of the carbon cluster pursuant to an embodiment.

Figs. 10A and 10B show a carbon nanotube as the nucleus of the proton conductor, and Fig. 10C is a schematic view showing carbon fibers pursuant to an embodiment.
25

Fig. 11 is a schematic sectional view showing an electrochemical device according to the present invention pursuant to an embodiment.

Fig. 12 is a schematic sectional view showing a gas storage device according to the present invention pursuant to an embodiment.

Fig. 13 is a schematic sectional view of outlet and inlet pressure detecting means connected to the gas storage device according to the present invention pursuant to an embodiment.

Fig. 14 is a schematic sectional view showing the gas storage device according to the present invention and a gas storage assist system connected thereto pursuant to an embodiment.

Fig. 15 is a schematic sectional view of another example of the gas storage device according to the present invention pursuant to an embodiment.

Fig. 16 is a schematic sectional view of a still another example of the gas storage device according to the present invention pursuant to an embodiment.

Fig. 17 is a schematic sectional view showing a gas storage device in which an electrochemical cell is formed in a multistage structure pursuant to an embodiment.

Fig. 18 is a schematic sectional view of another example of the gas storage device in which the electrochemical cell is formed in a multistage structure pursuant to an embodiment.

~~Best Mode for Carrying Out the Invention~~ DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a pressure reducing device, an electrochemical device, a pressure reducing and pressurizing device, a gas storage device, a gas storage assist system, and a method for driving these devices.

~~Now,~~Various embodiments of the present invention will be described by referring to the drawings.

A pressure reducing device according to the present invention ~~comprises,~~includes as shown in Fig. 2, an electrochemical cell 4 as a partition wall, having first and second catalytic electrodes 1 and 2 respectively forming first and second electrodes on which catalysts such as platinum are carried and a proton conductor 3 sandwiched in between the catalytic electrodes 1 and 2, and a high pressure vessel 5 and a low pressure vessel 6 disposed at both the sides of the electrochemical cell 4. A vacuum pump 8 is connected to the high pressure vessel

5 and the low pressure vessel 6 through a vacuum line 7. Further, an H₂ reservoir 9 and a gas flow meter 10 are connected to the high pressure vessel 5 and the low pressure vessel 6. To each of the vessels 5 and 6, lead introducing terminals 11 and 12 are connected. To the end of the gas flow meter 10, a power generation device using hydrogen gas as fuel, whose illustration is omitted, is connected.

Firstly, valves 13, 14 and 17 were closed to open valves 15 and 16 and obtain a vacuum in the high pressure vessel 5 and the low pressure vessel 6 by using the vacuum pump 8. Then, the valves 15 and 16 were closed to open the valves 13 and 14 and introduce the hydrogen gas of 10 atmospheric pressure to each of the vessels 5 and 6 by the H₂ reservoir 9. After that, the valves 13 and 14 were closed. Then, the valve 17 was opened to have only the low pressure vessel 6 of 1 atm.

At this time, when a voltage difference between the lead introducing terminal 11 and 12 connected to both the ends of the electrochemical cell 4 was measured, the voltage difference was about 100 mV.

Then, both the electrodes 1 and 2 of the electrochemical cell 4 were short-circuited to measure the change of pressure of the high pressure vessel 5. Fig. 3 is a graph showing the change of pressure of the high pressure vessel 5 with the lapse of time. As shown in Fig. 3, it was recognized that the pressure in the high pressure vessel 5 decreased with the lapse of time *t* and the short-circuit between both the electrodes 1 and 2 by a relay functioned.

The proton conductor 3 is desirably composed of a derivative formed in such a way that a material made of at least one kind, ~~selected from a group including~~ such as fullerene molecules, a cluster having carbons as a main component and a tubular or linear carbon structural body or the like, is prepared as a main component and a proton dissociation group is introduced to carbon atoms forming the material. ~~Other inventions~~ Additional embodiments described below are the same as the above.

Here, the proton dissociation group means a functional group in which protons can be separated in accordance with an electrolytic dissociation. The

dissociation of the protons means that the protons are separated from the functional group in accordance with the electrolytic dissociation.

The fullerene molecules as a nucleus of an object to which the proton dissociation group is introduced may be any spherical shell type cluster molecules Cm where (m indicates a natural number in which Cm may form a spherical shell structure.) without a special limitation. ~~Ordinarily~~In an embodiment, a single material of fullerene molecules selected from C36, C60, C70, C76, C78, C80, C82, C84, C86, C88, C90, C92, C94, C96, ~~etc.~~ or the mixture of two kinds or more materials ~~of them is~~thereof are preferably employed.

The fullerene molecules were found in the mass spectrometry spectrum of a cluster beam of carbons by a laser ablation in 1985 (Kroto, H.W.; Heath, J. R.; O'Brien, S.C.; Curl, R.F.; Smalley, R.E. Nature 1985. 318, 162.). ~~Actually, a~~A producing method was established about five years later. In 1990, a producing method of a carbon electrode by an arc discharge method was found in 1990. Then, fullerene has been paid attention to as a carbon semiconductor material or the like since then.

As shown in Figs. 4A and 4B, as Fullerenol having a structure formed by adding a plurality of hydroxyl groups to fullerene molecules, a synthesized example was firstly reported by Chiang et al. in 1992 (Chiang, L.Y.; Swirczewski, J.W.; Hsu, C.S.; Chowdhury, S.K.; Cameron, S.; Creegan, K., J. Chem. Soc, Chem. Commun. 1992, 1791).

When the inventors of the present invention used the fullerenol as an aggregate as shown in Fig. 5A to generate a mutual interaction between hydroxyl groups of the fullerenol molecules (in the drawing, \circ represents a fullerene molecule-) which come into close contact with each other, they could initially recognize that the aggregate exhibited high proton conductive characteristics as a macro aggregate, that is, the aggregate exhibited the dissociation characteristics of H^+ from the phenolic hydroxyl groups of the fullerenol molecules.

According to the present invention, the aggregate of fullerene having, for instance, a plurality of $-OSO_3H$ groups except fullerenol can be used as the ion conductor. Polyhydroxylated fullerene as shown in Fig. 5B in which an OH group

is replaced by an OSO_3H group, that is, hydrogensulfate esterified fullerenol was also reported by Chiang et al. in 1994 (Chiang, L.Y.; Wang, L.Y.; Swirczewski, J.W.; Soled, S.; Cameron, S., J. Org. Chem. 1994, 59, 3960). In the hydrogensulfate esterified fullerene, one molecule may include only OSO_3H groups or may include
5 a plurality OSO_3H groups and hydroxyl groups, respectively.

When a lot of the above-described fullerenols and hydrogensulfate esterified fullerenols are aggregated, a proton conductivity shown by them as a bulk is directly related to the movement of protons derived from a large quantity of hydroxyl groups or OSO_3H groups originally included in the molecules.
10 Accordingly, the fullerenols and the hydrogensulfate esterified fullerenols can be continuously employed even under an atmosphere of low humidity.

The fullerene constituting the base of these molecules especially has electrophilic characteristics, which is considered to greatly contribute to the acceleration of the electrolytic dissociation of hydrogen ions not only in OSO_3H groups high in acidity, but also in hydroxyl groups and exhibits an excellent proton
15 conductivity. Since a relatively large quantity of hydroxyl groups and OSO_3H groups can be introduced to one fullerene molecule, the density of the proton conductor related to conduction per unit volume becomes very high. Thus, a substantial conductivity is realized.

Most of the fullerenol and the hydrogensulfate esterified fullerenol are composed of fullerene carbon atoms, they are light and hardly deteriorated and include effectively no contaminated material. The production cost of fullerene is being rapidly lowered. The fullerene is considered to be a substantially ideal carbon material more than any other materials from the viewpoints of resources,
20 environment and economy.

Further, the proton dissociation group does not need to be limited to the above-described hydroxyl group or the OSO_3H group.

That is, the proton dissociation group is represented by a formula $-\text{XH}$. X may be an arbitrary atom or an atomic group having a bivalent bond. Further, this
30 group is represented by a formula $-\text{OH}$ or $-\text{YOH}$. Y may be an arbitrary atom or an atomic group having a bivalent bond.

Specifically, as the proton dissociation group, any one of -COOH, -SO₃H, -OPO(OH)₂, and -C₆H₄-SO₃H except in addition to -OH and -OSO₃H is preferable.

To synthesize fullerenol usable in the present invention, for instance, well-known processes such as acidification or hydrolysis are suitably combined and
5 applied to fullerene powder, so that desired groups can be introduced to carbon atoms forming the fullerene molecules.

Then, an obtained fullerene derivative is formed in the configuration of a film by an application or a deposition method to be used for the proton conductor 3 of the electrochemical cell 4.

10 The proton conductor 3 may be substantially composed of only the fullerene derivative or the fullerene derivative may be bonded by a binding agent.

When the proton conductor 3 is substantially composed of only the fullerene derivative, a film shaped proton conductor 3 formed by molding the fullerene derivative under pressure may be used. When the fullerene derivative bonded by
15 the binding agent are used as the proton conductor 3, the proton conductor with an adequate strength can be formed by the binding agent.

As polymer materials usable as the binding agent, one kind or two or more kinds of polymers having well-known film forming characteristics are employed. The proton conductor having such a structure can exhibit the same proton
20 conductivity as that of the proton conductor composed of only the fullerene derivative.

Further, the film forming characteristics resulting from the polymer materials are given to the proton conductor differently from the proton conductor made of only the fullerene derivative. Thus, the proton conductor formed by
25 bonding the fullerene derivative using the binding agent can be used as a flexible proton conductor 3 higher in its strength than a compression-molded product of the powder of the fullerene derivative and having a gas permeation preventing function. A proton conductive thin film used at this time has the thickness of about 300 μm or smaller.

30 As the polymer materials, any of materials that do not hinder the conductivity of protons (due to a reaction with the fullerene derivative) as much as

possible and have film forming characteristics may be used without a special limitation. Ordinarily, a material having no electronic conductivity and having a good stability is used. As specific examples, polyfluoroethylene, polyvinylidene fluoride, polyvinyl alcohol, ~~etc.~~and the like may be exemplified. These materials
5 are preferable polymer materials from reasons described below.

Firstly, since polytetrafluoroethylene can more easily form a thin film having higher strength with a smaller amount of mixing than other polymer materials, the polytetrafluoroethylene is preferable. In this case, the amount of mixing is about 3 wt% or less and preferably an amount as small as about 0.5 to
10 about 1.5 wt%. The thickness of the thin film can be ordinarily reduced to about 100 μm to about 1 μm .

Polyvinylidene fluoride or polyvinyl alcohol is preferable, because the proton conductive thin film having the excellent gas permeation preventing function can be obtained. In this case, the amount of mixing is preferably located
15 within a range of 5 to 15 wt%.

When each of the amount of mixing of polyfluoroethylene, polyvinylidene fluoride or polyvinyl alcohol is lower than the lower limit value of the above-described range, an adverse effect may be possibly given to a film formation.

In order to obtain the thin film of the proton conductor formed by bonding
20 the fullerene derivatives respectively by the binding agent, a well-known film forming method such as a pressure molding method or an extrusion molding method may be employed.

In the device according to the present invention, the electrodes 1 and 2 and the fullerene derivative as the proton conductor 3 are preferably formed in flexible
25 sheet shapes having a physically adequate strength in view of treatment and compactness.

Since the electrochemical cell 4 can effectively function in atmospheric air, even when temperature or humidity during an operation is not adjusted, the pressure of the hydrogen gas can be efficiently reduced.

30 The fullerene derivative formed by introducing the proton dissociation group to the carbon atoms forming fullerene molecules such as fullerenols is used

as a material for forming the proton conductor 3. Thus, the electrochemical cell 4 can function in the atmospheric air under a state of low humidity even when there is no humidifier, differently from a case that Nafion as an H_3O^+ ion conductor is used.

That is, since the pressure of the hydrogen gas can be reduced in the atmospheric air under the state of low humidity, an initial operation can be accelerated upon reducing the pressure of hydrogen without requiring a time until a steady operation. For instance, the humidifier may be provided to similarly reduce the pressure of the hydrogen gas under the presence of water. However, the present invention does not essentially require the above-described conditions.

When Nafion as the H_3O^+ ion conductor is used, hydrogen is compressed and water is also generated, so that a dehumidifier is necessary. As compared therewith, in this embodiment of the present invention, even when the dehumidifier is not provided, the pressure of the hydrogen gas can be reduced.

Further, even when the humidifier is not provided, an electrochemical pressure reducing operation can be efficiently realized. Thus, the content of water of the hydrogen gas whose pressure is reduced is small. Accordingly, a dehumidifying process as a post-process can be made unnecessary.

Therefore, the electrochemical cell 4 can efficiently reduce the pressure of the hydrogen gas. The device according to the present invention is more compact and highly generalized.

In the present invention, as the proton conductor, for instance, a cluster derivative, can be used in place of the fullerene derivative, which is obtained in such a way that a cluster made of carbon powder is obtained by an arc discharge method of a carbon electrode, the carbon powder is acidified and a proton (H^+) dissociation group is introduced to the carbon powder.

Here, the cluster ordinarily means an aggregate formed by bonding or aggregating together several to several hundred atoms. The aggregate enables a proton conductivity to be improved, holds chemical characteristics to have adequate film strength and is liable to easily form a layer. This cluster indicates the aggregate that includes carbons as main components and is formed by bonding several to several hundred carbon atoms irrespective of kinds of carbon to carbon

bonds. However, the cluster is not necessarily composed of only carbons of 100 % and other atoms may be mixed therein. The aggregate that many carbons occupy including the above-described case is called a carbon cluster.

5 Since the above-described proton conductor includes, as a main component, a material obtained by introducing the proton dissociation group to the carbon cluster as a nucleus, the proton is easily dissociated under a dry state. Thus, effects similar to those of the above-described proton conductor as well as the proton conductivity can be realized. Since many kinds of carbonaceous materials as described below are included in the category of the above-described carbon cluster,
10 a range of selection of the carbonaceous material is effectively wide.

In this case, the carbon cluster is used as the nucleus, because a large quantity of proton dissociation groups needs to be introduced to obtain good proton conductivity and the above-described thing can be realized by the carbon cluster. Thus, the acidity of a solid proton conductor is extremely high. However, the
15 carbon cluster is hardly oxide deteriorated differently from other ordinary carbonaceous materials, excellent in its durability and component atoms are tightly bonded together. Accordingly, even when the acidity is high, the bonds between the atoms do not collapse, that is, the carbon cluster is hardly chemically changed and can maintain a film structure.

20 The proton conductor having such a structure can also exhibit the high proton conductivity even under a dry state. As shown Figs. 6 to 9, there are various kinds of carbon clusters. As the materials of the proton conductor, a selection range is widened.

Firstly, various kinds of carbon clusters are shown in Figs. 6A to 6M, which
25 include many carbon atoms aggregated and having spherical or long spherical structures or closed surface structures similar thereto. In this case, molecular fullerene is shown together therewith. On the other hand, various kinds of examples of carbon clusters are shown in Figs. 7A to 7D, in which the spherical structures are partly deficient. The carbon clusters shown herein are characterized
30 in that open ends are provided in the structures. Most of the structures are produced as by-products in the production processes of fullerene by an arc discharge method.

When most of the carbon atoms of the carbon cluster are bonded in SP³, various kinds of clusters having the structures of diamond are produced as shown in Figs. 8A to 8G. In Figs. 7C and 7D, painted-out parts in black show a five-membered ring or a seven-membered ring.

5 The clusters in which the carbon atoms are substantially bonded in SP² have plane structures of graphite or all or a part of the structures of fullerene or a nanotube. Since the clusters having the graphite structures of them substantially have an electronic conductivity therein, these clusters are not preferable as the nucleus of the proton conductor.

10 On the other hand, since the clusters having the SP² bonds of fullerene or the nanotube partly include a factor of the SP³ bonds, most of them do not have the electronic conductivity, so that these clusters having the SP² bonds are preferable as the nucleus of the proton conductor.

 Figs. 9A to 9G show various kinds of cases that clusters are bonded
15 together. Such structures may be applied to the present invention. In Figs. 9A and 9B, ~ indicates a bond chain such as (CH₂)_n, (CF₂)_n or the like. Further, in Figs. 9E to 9G, painted-out parts in black represent five-membered rings or seven-membered rings.

 In the present invention, the above-described proton dissociation group
20 needs to be introduced to carbon atoms forming the carbon cluster. As means for introducing the proton dissociation group, a below-described producing method is preferable.

 That is, the carbon cluster made of carbon powder is firstly produced by the arc discharge of the carbon electrode. Subsequently, the carbon cluster is acidified,
25 or a process such as a hydrolysis is further performed or a sulfonation is further performed or phosphate esterification is suitably formed. Thus, a carbon cluster derivative as a desired product can be easily obtained. In the above-described acidifying process, sulfuric acid or the like is used.

 The carbon cluster can be directly formed in the shape of a film, pellets or
30 the like under pressure without a binder. In the present invention, the carbon cluster as the nucleus preferably has the length of a major axis of 100 nm or shorter,

especially preferably 100 Å or lower and the number of groups introduced thereto is desirably 2 or more.

As the carbon cluster, a cage type structure of fullerene or the like or a structure having open ends in at least a part thereof is preferable. Fullerene having such a defective structure has the reactivity of fullerene. At the same time, the defective part, that is, the opening part additionally has a higher reactivity. Accordingly, acid (proton) dissociation substituent groups are promoted to be introduced by the acidifying process to obtain a higher substituent introduction rate and a high proton conductivity. Further, a larger quantity of fullerene with the above-described structure can be synthesized than ordinary fullerene and produced at an extremely low cost.

On the other hand, as the nucleus of the proton conductor of the present invention, the tubular or the linear carbon structure is preferably used. As the tubular carbon structure, a tube shape, for instance, a carbon nanotube is preferably used. As the linear carbon structure, a fiber type shape, for instance, a carbon fiber is preferably used.

The carbon nanotube or the carbon fiber is apt to structurally easily discharge electrons and can greatly increase its surface area. Thus, the carbon nanotube or the carbon fiber can more improve a proton propagation efficiency.

Here, the preferably usable carbon nanotube or the carbon fiber can be produced by the arc discharge method or a chemical gas phase deposition method (a thermal CVD method).

In the arc discharge method, a metal catalyst such as FeS, Ni, Co, ~~etc.~~ or the like is used and a carbon nanotube or carbon fiber material is synthesized under an atmosphere of He, for instance, an atmosphere of 150 Torr by using an arc discharge chamber. The carbon nanotube material is stuck to the inner surface of the chamber in the shape of a cloth in accordance with an arc discharge. Thus, for instance, the carbon nanotube can be obtained. In this case, when the catalyst coexists, the carbon nanotube having a small diameter can be obtained. When the arc discharge is carried out under the condition of having no catalyst, the thick carbon nanotube having many layers can be obtained.

As described above, the carbon nanotube can be produced by, for instance, carrying out the arc discharge under the condition of having no catalyst. A multi-layer carbon nanotube 101 shown in Fig. 10A and a multi-layer carbon nanotube 201 with a graphene structure (a cylindrical structure) shown in Fig. 10B is known as a high quality carbon nanotube having no defect and having a very high performance as an electron discharging material.

The proton dissociation group can be introduced to the carbon nanotube obtained as described above by the arc discharge method in the same processes as mentioned above. Thus, a proton conductor excellent in its proton conductivity even under a dry state can be obtained.

The chemical gas phase deposition method is a method for synthesizing the carbon nanotube or the carbon fiber by allowing fine particles of transition metals to react with hydrocarbons or CO of acetylene, benzene, ethylene, ~~etc~~ and the like. A transition metal base or a coat base is allowed to react with hydrocarbon gas or CO gas to accumulate the carbon nanotube or the carbon fiber 301 on the base 300 as shown in Fig. 10C.

For instance, an Ni base 300 is disposed in an alumina tube heated at about 700°C and allowed to react with toluene/H₂ gas (for instance, 100 sccm) so that the carbon fiber 301 having the structure as shown in Fig. 10C can be synthesized.

Here, the aspect ratio of the carbon nanotube preferably ranges from about 1 : 1000 to about 1 : 10. Further, the aspect ratio of the carbon fiber preferably ranges from about 1 : 5000 to about 1 : 10. The diameter of the tubular or linear carbon structure is preferably located within a range of about 0.001 to about 0.5 μm. The length is preferably about 1 to about 5 μm.

In the device according to the present invention, only the single electrochemical cell serving as a pressure partition wall may be disposed. However, a plurality of electrochemical cells may be arranged in parallel in a gas flowing direction and may have a multistage structure. Especially, when the difference of pressure of the vessels disposed at both the sides of the electrochemical cell is large, several electrochemical cells need to be used.

The present invention concerns an electrochemical device. The electrochemical device ~~comprises~~includes a pressure reducing part including an electrochemical cell having a first electrode for decomposing hydrogen gas into protons, a second electrode for converting the protons produced in the first
5 electrode into the hydrogen gas again and a proton conductor sandwiched in between both the electrodes and a high pressure vessel disposed in the first electrode side of the electrochemical cell to accommodate a gaseous material including the hydrogen gas; the electrochemical cell functioning to reduce pressure in the high pressure vessel; and a gas consuming part including a hydrogen gas
10 storage part disposed in contact with the second electrode side in the pressure reducing part, a third electrode disposed in contact with the hydrogen storage part for decomposing the hydrogen gas supplied from the hydrogen gas storage part into protons; a fourth electrode for converting the protons generated in the third electrode into water, and a proton conductor sandwiched in between both the
15 electrodes, the protons being converted into water in the fourth electrode to take out electrochemical energy between the third electrode and the fourth electrode.

As a method for driving the electrochemical device according to the present invention, for instance, when the pressure reducing part is driven, the electrochemical cell functions to reduce pressure in the high pressure vessel and the
20 hydrogen gas storage part is disposed in contact with the second electrode side in the pressure reducing part. The gas consuming part including the third electrode for decomposing the hydrogen gas supplied from the hydrogen gas storage part into protons; the fourth electrode for converting the protons generated in the third electrode into water, and the proton conductor sandwiched in between both the
25 electrodes is desirably disposed in contact with the hydrogen gas storage part to convert the protons into water in the fourth electrode and take out the electrochemical energy between the third electrode and the fourth electrode.

In the electrochemical device according to the present invention, since a mechanical movable part is not provided in the electrochemical device like the
30 above-described gas pressure regulator according to the present invention, a compact, durable and silent device can be realized.

A specific structure of the electrochemical device according to the present invention is shown in Fig. 11.

As shown in Fig. 11, a pressure reducing part 18 includes an electrochemical cell 4 having a first electrode 1 for decomposing hydrogen gas into protons, a second electrode 2 for converting the protons produced in the first electrode 1 into the hydrogen gas again and a proton conductor 3 sandwiched in between both the electrodes 1 and 2, and a high pressure vessel 5 disposed in the first electrode 1 side of the electrochemical cell 4 to accommodate a gaseous material including the hydrogen gas. The electrochemical cell 4 functions to reduce pressure in the high pressure vessel 5. A hydrogen gas storage part 19 is disposed in contact with the second electrode 2 side of the pressure reducing part 18. A gas consuming part 20 is disposed in contact with the hydrogen gas storage part 19 and includes a third electrode 21 disposed in contact with the hydrogen storage part 19 for decomposing the hydrogen gas supplied from the hydrogen gas storage part 19 into protons, a fourth electrode 22 for converting the protons generated in the third electrode 21 into water, and a proton conductor 23 sandwiched in between both the electrodes 21 and 22. The protons can be converted into water in the fourth electrode 22 and electrochemical energy can be taken out between the third electrode 21 and the fourth electrode 22 to serve as a fuel cell part. In the surface side of the fourth electrode 22 that does not come into contact with the proton conductor 23, O₂ or O₂ containing gas is supplied.

A pressure sensor 24 is disposed in the hydrogen gas storage part 19. The pressure sensor 24 serves to interlock with a relay switch 11a connected between lead introducing terminals 11 and 12 connected between the first and second electrodes 1 and 2 of the electrochemical cell 4 to compensate for the consumption of gas.

The high pressure vessel 5 is connected to an H₂ supply tank 25 through a valve 25a. When pressure in the high pressure vessel 5 reaches a prescribed value or smaller, the valve 25a is opened so that hydrogen gas can be supplied from the H₂ supply tank 25. The H₂ supply tank 25 may be filled with a hydrogen gas storing alloy, a hydrogen gas storing carbon material, metal halide, etc. As the

hydrogen gas storing alloys, LaNi_6 , CaNi_5 , $\text{TiCo}_{0.5}\text{Mn}_{0.5}$, $\text{TiCo}_{0.5}\text{Fe}_{0.5}$, $\text{TiFe}_{0.8}\text{Ni}_{0.15}\text{V}_{0.05}$, etc. may be employed. As the hydrogen gas storing materials, carbon materials, carbon nanotubes, carbon fibers, activated carbons, etc. may be employed. As the metal halides, NaAlH_4 , LiAlH_4 , etc. may be employed.

5 The high pressure vessel 5 may be also filled with the hydrogen gas storing alloy, the hydrogen gas storing carbon material, the metal halide, ~~ete~~and the like.

In this case, since the gas interrupting characteristics of the proton conductors 3 and 23 must be high, the proton conductors 3 and 23 need to have characteristics in which ionized gas is permeated, however, gas itself is not permeated. To realize the above-described characteristics, the proton conductors 3 and 23 are desirably composed of a derivative formed in such a way that at least one kind of material selected from a group including fullerene molecules, a cluster having carbons as a main component, and a tubular or linear carbon structure is included as a main component, and a proton dissociation group is introduced to carbon atoms forming this material in the same manner as described above.

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The present invention concerns a gas storage device ~~comprising~~including a gas inlet and outlet part for introducing or discharging gas; a gas storage part for storing gas; an electrochemical cell disposed in the gas storage part and including a first electrode for decomposing the gas into ions, a second electrode for converting the ions generated in the first electrode into the gas again and an ion conductor sandwiched in between both the electrodes; and a pressure reducing and pressurizing part in which the gas is supplied to or discharged from the gas storage part through the gas inlet and outlet part in accordance with the function of the electrochemical cell to decrease or increase pressure in the gas storage part.

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As a method for driving the gas storage device according to the present invention, for instance, when the gas storage device is driven, the gas is desirably supplied to or discharged from the gas storage part through the gas inlet and outlet part in accordance with the function of the electrochemical cell to decrease or increase pressure in the gas storage part.

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In the gas storage device according to the present invention, since a mechanical movable part is not provided in the gas storage device like the above-

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described gas pressure regulator or the electrochemical device according to the present invention, the compact and durable gas storage device can be realized.

A gas storage device 26 according to the present invention has a structure as shown in Fig. 12. A gas inlet and outlet part 27 provided in the gas storage device 26 has an opening for inputting and outputting gas and a micro space sufficient for temporarily holding gas under equal pressure.

Inlet and outlet pressure detecting means 28 is provided for detecting pressure in the micro space and is, for instance, a pressure sensor using a diaphragm. As one example of such a pressure sensor, for instance, a pressure sensor having a diaphragm 29, a closed space 30 in which a prescribed quantity of gas is sealed and a micro-switch 31 as shown in Fig. 13 is used.

One surface side of the diaphragm 29 has the same pressure as that of the gas inlet and outlet part 27. Thus, the diaphragm 29 is moved until the differential pressure of the pressure of the closed space 30 and the pressure of the gas inlet and outlet part 27 is balanced to the resilient force of the diaphragm 29. When the pressure of the gas inlet and outlet part 27 reaches prescribed pressure, the micro-switch 31 is switched from ON (a connected state) to OFF (a disconnected state).

A pressure wall 32 is a pressure resistant wall for holding high pressure, for instance, 10 to 300 atmospheric pressure and has a gas moving hole as many openings with very small areas in the boundary of the gas inlet and outlet part 27 and the pressure wall 32. The form of the pressure wall 32 is not especially limited to a specific form, however, to uniformly distribute the pressure, a cylindrical form or a spherical form is more preferable. Fig. 12 shows a sectional view taken along a plane including the center of a cylinder when the form of the pressure wall 32 is a cylindrical form.

The gas moving hole holds a first electrode 1, an ion conductor 3 and a second electrode 2 against the pressure of a gas storage part 33, and at the same time, can move gas from the gas storage part 33 to the gas inlet and outlet part 27. An electrochemical cell including the first electrode 1, the ion conductor 3 and the second electrode 2 is a pressure reducing and pressurizing part operating as

independent parts and the entire part of the electrochemical cell is held in the gas storage part 33.

Lead lines 34 and 35 are electric conductors having their one ends respectively connected to the second electrode 2 and the first electrode 1. The other ends of the lead lines are connected to a second electrode terminal 38 and a first electrode terminal 39 while insulation from the pressure wall 32 is maintained. A connecting line 36 and a connecting line 37 connects respectively the contacts of the second electrode terminal 38 and the first electrode terminal 39 and the micro-switch 31 together.

The gas storage device 26 according to the present invention includes a gas storage assist system. The gas storage assist system desirably comprises a gas passage for supplying the gas to the gas inlet and outlet part 27 provided in the gas storage device 26; a pressure detecting means for detecting gas pressure in the gas passage 41; a voltage detecting means for detecting voltage generated between the first electrode 1 and the second electrode 2; a calculating means for calculating a control current signal on the basis of the gas pressure and the voltage; a current supply means for generating a control current; and a switching means for alternately switching a state that the control current is supplied between the first electrode 1 and the second electrode 2 and a state that the voltage is detected until the voltage reaches a predetermined value.

The gas storage device 26 having the gas storage assist system 40 according to the present invention is shown in Fig. 14. A part shown by a broken line in Fig. 14 represents the gas storage device 26 and a part shown by a full line represents the gas storage assist system 40.

The passage 41 has a structure connected to the opening part of the gas inlet and outlet part 27 provided in the gas storage device 26 so that gas does not leak. The gas is supplied to the passage 41 from a tank 47.

A pressure detecting mechanism 42 ~~is means for detecting~~ can detect the pressure value of the gas in the passage 41, and, for instance, changes the displacement of a diaphragm to a resistance value to an analog pressure value of P1. The pressure detecting mechanism 42 is provided for the purpose of detecting

the pressure of the gas inlet and outlet part 27 of the gas storage device 26, that is, the pressure applied to the second electrode 2 from the gas inlet and outlet part 27 side. Since the passage 41 is connected to the gas inlet and outlet part 27, they have the substantially same pressure. The pressure detecting mechanism 42 is provided
5 in the vicinity of the passage 41, this purpose can be achieved.

A first terminal 48 and a second terminal 49 hold an electric contact with the first electrode terminal 39 and the second electrode terminal 38 of the gas storage device 26.

A switching part 46 is switching means connected to the first terminal 48
10 and the second terminal 49 by electric conductive lines.

Contacts S0 and S1, and contacts S3 and S4 are turned on at the same time. When a switching signal C1 is changed, contacts S0 and S2, and contacts S3 and S5 are turned on at the same time. The switching signal C1 is transmitted from a calculating part 44. When switching members 43a and 44a of a switch are
15 connected to the contacts S1 and S4, a pressure voltage detecting part 43 detects voltage generated between the first electrode 1 and the second electrode 2. When the switching members 43a and 44a of the switch are connected to the contacts S2 and S5, prescribed current is supplied to the first terminal 48 and the second terminal 49 from a current supply part 45.

20 The direction and the quantity of the current are determined by a current control signal C2 and the values are calculated by the calculating part 44.

An operation upon discharging gas in the gas storage device 26 is carried out as described below in the same manner as that of the pressure reducing device according to the present invention.

25 Voltage corresponding to the pressure difference between the storage part 33 and the gas inlet and outlet part 27 is generated between the first electrode terminal 39 and the second electrode terminal 38 of the gas storage device 26 and guided to the respective contacts of the micro-switch 31 via the connecting line 36 and the connecting line 37. When the pressure of the gas inlet and outlet part 27 is
30 lowered to a prescribed value or smaller, the contact of the micro-switch 31 is turned ON. Thus, current is supplied to the second electrode 2 and the first

electrode 1 on the basis of the generated voltage and ions are supplied to the ion conductor 3. As a result, the pressure of gas in the gas storage part 33 is reduced and the pressure reduced gas is supplied to the gas inlet and outlet part 27. When the gas inlet and outlet part 27 is sufficiently filled with the gas, the contact of the micro-switch 31 is turned OFF to interrupt the current of the second electrode 2 and the first electrode 1. Consequently, the conduction of the ions is interrupted to stop the entry of the gas in the gas storage part 33 to the gas inlet and outlet part 27.

As a contact form of the micro-switch 31, when a switch of a type that hysteresis characteristics, namely, different pressure allows the switch to shift to each of states of ON/OFF is used, the ON/OFF operations of the switch can be slowly repeated within a prescribed range of pressure change. Thus, the life of the contact of the switch can be effectively lengthened.

Thus, since the gas inlet and outlet part 27 is filled with gas of prescribed pressure, the gas of the prescribed pressure can be taken out from an opening part. In the processes of the operation, external electric power is not required, so that the gas storage device high in its reliability and easy in its maintenance can be provided.

Now, an operation of the gas storage device 26 upon storing gas will be described by referring to the above-described Figs. 12 to 14.

When the gas is stored, the gas storage device 26 is connected to the gas storage assist system 40 to store the gas.

The connecting line 36 and the connecting line 37 of the gas storage device 26 are temporarily removed or one of the connecting lines is disconnected by a switch which is provided halfway and is not illustrated. Then, the passage 41 is connected to the opening part of the gas inlet and outlet part 27, and the first terminal 48 and the second terminal 49 are connected to the first electrode terminal 39 and the second electrode terminal 38.

The switching part 46 is switched to a pressure detecting operation side by the switching signal C1 and pressure voltage is detected by the pressure voltage detecting part 43. Here, pressure in the second electrode 2 is detected as an output P1 from the pressure detecting mechanism 42. Accordingly, the pressure of gas in

the gas storage part 33 is obtained as P2 by substituting the obtained values for the above-mentioned formula (1).

When the pressure P2 is lower than the withstanding pressure of the pressure wall 32 of the gas storage part 33, even if the gas storage part is further filled with gas, the pressure wall 32 is not broken. Thus, the gas storage part can be further filled with the gas. To move the gas to the gas storage part 33, the switching part 46 may be switched by the switching signal C1 to supply current and a prescribed current in an opposite direction to that of the current upon discharging the gas may be applied to the second electrode 2 and the first electrode 1.

When the intensity of the current more increases, an amount of movement of gas more increases, so that the gas storage part can be rapidly filled with the gas. However, when excessive current is supplied, the ion conductor 3 may be possibly broken. Therefore, the current needs to be located within a limited range.

As the prescribed current, a constant current may be supplied throughout all period of filling of gas, or a quantity of current may be arbitrarily controlled in accordance with the progress of the filling of gas.

The switch of the switching part 46 is alternately switched to alternately fill the storage part 33 with gas and monitor the pressure of the storage part 33. Thus, the pressure of the gas in the storage part 33 can be raised until prescribed pressure is finally obtained.

Thus, while the pressure of the storage part 33 is monitored without providing the pressure sensor in the storage part 33, the storage part 33 can be safely filled with the gas. Accordingly, the structure of the storage part 33 can be effectively simplified. Further, in the gas storage assist system 40 side, since a part under a high pressure state does not exist, the gas storage assist system 40 itself can be made inexpensive and can be safely used in an ordinary home at the same time.

Fig. 15 shows an example in which other electrochemical cell is provided in the gas storage device 26 shown in Fig. 12. Since members designated by the same reference numerals as those shown in Fig. 12 are the same members having the same operational functions, the detailed description thereof is omitted.

A third electrode 21 is provided in contact with the opening part of a gas inlet and outlet part 27. A second proton conductor 23 is disposed between the third electrode 21 and a fourth electrode 22. A third terminal 50 is electrically connected to the third electrode 21. A fourth terminal 51 is connected to the fourth electrode 22. An arrow mark shown by 52 indicates that liquid material or gaseous material is supplied to the fourth electrode 22.

Now, an operation of the gas storage device shown in Fig. 15 will be described below.

When specific materials are supplied to the third electrode 21 and the fourth electrode 22, the gas storage device according to the present invention shown in Fig. 15 can serve as a fuel cell in accordance with the actions of the third electrode 21, the proton conductor 23 and the fourth electrode 22. Here, in accordance with the materials respectively supplied to electrode films, the third electrode 21 serves as an anode or a cathode and the fourth electrode 22 serves as a cathode or an anode. For instance, when hydrogen gas is supplied to the third electrode 21 and air (oxygen containing gas) or oxygen gas is supplied to the fourth electrode 22, the third electrode 21 serves as the anode and the fourth electrode 22 serves as the cathode. Thus, negative voltage can be obtained from the third terminal 50 and positive voltage can be obtained from the fourth terminal 51.

The operation until the gas of prescribed pressure is obtained in the gas inlet and outlet part 27 is the same as described above.

When the positive voltage is applied to the fourth terminal 51 and the negative voltage is applied to the third terminal 50 and pure water or water vapor is supplied to the fourth electrode 22, the hydrogen gas can be obtained in the gas inlet and outlet part 27. An operation that the hydrogen gas in the gas inlet and outlet part 27 is pressurized to store the gas in the gas storage part 33 is the same as described above.

This device is a compact and portable device capable of producing gas such as hydrogen gas and generating power. Accordingly, the device is useful for using electric power in outdoors and for a power supply for emergency.

Fig. 16 shows a gas storage device 126 having a display part 53 for displaying the state of the gas storage device 26. The above-described state indicates, for instance, the pressure in the gas storage part 33, the filled state of the gas in the gas storage part 33, the remaining quantity of gas, or whether or not the electrochemical cell having the first electrode 1 and the second electrode 2 carrying catalysts for ionic bond or ionic dissociation normally functions, etc.

When the pressure of the gas inlet and outlet part 27 is understood from the formula of Nernst represented by the above-described formula (1), the pressure of the gas storage part 33 can be recognized. When the gas storage device 26 operates, the gas inlet and outlet part 27 is maintained to prescribed pressure in accordance with the operation of the pressure detecting means 28. Thus, the pressure of the gas storage part 33 can be grasped.

The pressure of the gas storage part 33 also shows the filled state of the gas in the gas storage part 33 at the same time. Since the reduction of pressure in the gas storage part 33 means the decrease of the quantity of filled gas, the filled state or the remaining quantity of gas can be recognized thereby.

When the electrochemical cell normally operates while the device operates, the micro-switch 31 provided in the pressure detecting means 28 repeats ON/OFF operations. Accordingly, when the operations are detected, it can be decided whether or not the operation of the electrochemical cell is normal.

The display part 53 is composed of, for instance, a voltmeter or a light emitting element such as an LED. A connecting line 54 is connected to the second electrode 2 and a connecting line 55 is connected to the first electrode 1. A connecting switch 56 is connected on the way thereto. Only when the display part 53 is used, a push button 57 is pressed to connect a circuit. The display part 53 may be ordinarily disconnected from an electrode film.

When the display part 53 is the voltmeter, the pointer of the voltmeter swings in accordance with the ON/OFF operations of the micro-switch 31. At the time of ON, since the first electrode 1 and the second electrode 2 are short-circuited, the pointer of the voltmeter points zero. At the time of OFF, voltage is generated, that is, voltage corresponding to a pressure difference is generated.

Although the internal resistance of the voltmeter is high, a little current is always continuously supplied between the electrodes. Thus, a very small quantity of gas flows out from the gas storage part 33. Thus, when a display is not requested, the display part 53 is desirably disconnected from the circuit. The display part 53 may be visually recognizable detecting means such as the LED or a buzzer as means depending on an auditory sense. An operating point is arbitrarily set by adjusting the light emission start voltage of the LED and the pressure of the gas storage part 33 by a resistance division, or setting the specification of winding of the buzzer.

Thus, the state of the gas storage device 26 can be displayed without requiring external electric power. A refilling time can be effectively estimated, the remaining quantity of gas can be effectively detected and the normal operation of the gas storage device 26 can be conveniently recognized.

Fig. 17 shows an example that a plurality of electrochemical cells are arranged in the gas storage device 26 to form a multistage structure.

High pressure gas is supplied to a high pressure side 58. Gas to be used is taken out from a low pressure gas side 59. Electrochemical cells 60 to 65 are arranged in such a way that empty chambers 66 to 70 are respectively arranged between the electrochemical cells. Each of the electrochemical cells has a proton conductor sandwiched in between two gas diffusion electrodes. A surface of the gas diffusion electrode that comes into contact with the proton conductor carries a catalyst.

A method for controlling each electrode of each electrochemical cell is the same as that of the previously described embodiment, a detailed explanation thereof is omitted.

In accordance with the device, the differential pressure at both the sides of each electrochemical cell is set to a prescribed constant value to sequentially perform a pressure reducing operation, so that a pressure difference applied to the single body of each electrochemical cell can be reduced. For instance, when six electrochemical cells are provided, assuming that the differential pressure applied to one electrochemical cell is 20 atmospheric pressure and the differential pressure

applied to the low pressure side 59 is one atmospheric pressure, the pressure of the high pressure side 58 may be 121 atmospheric pressure. Irrespective of the large pressure difference such as 120 atmospheric pressure, the pressure resisting force of the electrochemical cell may withstand 20 atmospheric pressure. Accordingly, the design of the device is advantageously simplified.

In the device shown in Fig. 17, the empty chambers are respectively provided between the electrochemical cells. However, when a function for detecting the pressure of the empty chambers is not necessary, such empty chambers are not necessarily required. Fig. 18 shows a schematic sectional view of a device in which empty chambers are not provided between electrochemical cells.

The basic structure of the electrochemical cells 71 to 76 is the same as that shown in Fig. 17. However, gas diffusion electrodes can be commonly used with gas diffusion electrodes of next stages. Accordingly, the number of the gas diffusion electrodes is decreased and the empty chambers are not provided between the electrochemical cells.

Now, an operation of this device will be described below.

Supplied hydrogen gas is electrically dissociated to electrons and protons due to the action of a catalyst 78 carried on the surface of a gas diffusion electrode 77. The electrically dissociated protons move throughout a proton conductor due to the action of a proton conductor 79. The protons are bonded to the electrons due to the action of a catalyst 81 carried on the surface of a gas diffusion electrode 80 to become the hydrogen gas again. The hydrogen gas is diffused in the gas diffusion electrode 80 having many pores through which the gas passes.

The hydrogen gas permeates the gas diffusion electrode 80 according to a concentration distribution and is electrically dissociated to the protons and the electrons again due to the action of a catalyst 82 carried on the other surface of the gas diffusion electrode 80. The electrically dissociated protons move due to the action of a proton conductor 83 to reach a gas diffusion electrode 84. The protons are returned to the hydrogen gas again in the gas diffusion electrode 84 due to the action of a catalyst 85 carried on the surface of the gas diffusion electrode 84.

The above-described processes are repeated to sequentially reduce pressure. Here, voltage is detected between the gas diffusion electrode 80 and the gas diffusion electrode 84 as described above. Accordingly, for instance, when both the electrodes are conducted to each other in accordance with the generated voltage to supply current to the gas diffusion electrode 80 and the gas diffusion electrode 84, the pressure difference between the gas diffusion electrode 80 and the gas diffusion electrode 84 can be maintained to a prescribed value. The pressure resistance of the gas diffusion electrodes and the proton conductors can be made substantially equal.

In this embodiment, an example that the hydrogen gas is used as gas is described. However, oxygen gas may be used. In this case, as the ion conductor, zirconium oxide is preferably employed.

The present invention is not limited to the above-described embodiments stated by referring to the drawings. It is apparent for a person with ordinary skill in the art that various changes, substitutions or equivalence thereto may be made without departing the attached claims and the gist thereof.

~~Industrial Applicability~~

According to the present invention, since the mechanical movable part is not provided in the device, the compact, durable and silent pressure reducing device, the electrochemical device, the pressure reducing and pressurizing device, the gas storage device and the gas storage assist system and a method for driving these devices can be realized.

The present invention is employed to make the device itself compact and portable. Thus, for instance, the electrochemical device that can be carried by an individual and can easily operate various devices driven by using gas such as hydrogen gas can be obtained.

It should be understood that various changes and modifications to the presently preferred embodiments described herein will be apparent to those skilled in the art. Such changes and modifications can be made without departing from the spirit and scope of the present invention and without diminishing its intended

advantages. It is therefore intended that such changes and modifications be covered by the appended claims.

ABSTRACT OF THE DISCLOSURE

~~The present invention relates to a~~ A gas pressure regulator and applications thereof are provided. ~~The gas pressure regulator including~~ es an electrochemical cell ~~(4)~~ having a first electrode ~~(1)~~ for decomposing gas into ions, a second
5 electrode ~~(2)~~ for converting the ions generated in the first electrode ~~(1)~~ into the gas again and an ion conductor ~~(3)~~ sandwiched in between both the electrodes ~~(1)~~ and ~~(2)~~; and a high pressure vessel ~~(5)~~ disposed in one side of the electrochemical cell ~~(4)~~. In this device, the gas is decomposed into the ions in the first electrode ~~(1)~~. The decomposed ions are allowed to pass through the ion conductor ~~(3)~~ sandwiched
10 in between the first electrode ~~(1)~~ and the second electrode ~~(2)~~ and conducted to the second electrode ~~(2)~~ side. The conducted ions are reconverted into the gas in the second electrode ~~(2)~~.

This listing of claims will replace all prior versions, and listings, of claims in the application:

Listing of claims:

5 Claims 1-24 (canceled)

 Claim 25 (new): A gas pressure regulator comprising:
 an electrochemical cell including a first electrode for decomposing a gas
 into one or more ions, a second electrode for converting the ions generated in the
10 first electrode into the gas again and an ion conductor sandwiched in between both
 the first and second electrodes; and
 a high pressure vessel disposed in one side of the electrochemical cell.

 Claim 26 (new): The gas pressure regulator according to claim 25,
15 further comprising a member for supplying a control current to both ends of the
 first electrode and the second electrode, wherein a quantity of the control current is
 controlled to control a flow rate of gas flowing across both the electrodes.

 Claim 27 (new): The gas pressure regulator according to claim 25,
20 wherein the gas includes hydrogen gas or oxygen gas.

 Claim 28 (new): The gas pressure regulator according to claim 25,
 wherein the ion conductor includes a film that includes an electrolyte material
 capable of permeating the ionized gas.

25 Claim 29 (new): The gas pressure regulator according to claim 25,
 wherein the first electrode and the second electrode includes an electrode film on
 which a catalyst capable of ionic equilibrium of the gas is carried.

30 Claim 30 (new): The gas pressure regulator according to claim 25,
 wherein a low pressure vessel is disposed in another side of the electrochemical

cell, and wherein the electrochemical cell serves as a gas partition wall and has a member for regulating pressure by controlling a potential between both the first and second electrode when a pressure difference is generated between both sides of the electrochemical cell.

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Claim 31 (new): The gas pressure regulator according to claim 30, wherein an electromotive force generated from the pressure difference is short-circuited or the pressure is regulated by a variable resistor.

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Claim 32 (new): The gas pressure regulator according to claim 25, wherein a plurality of electrochemical cells are arranged in parallel in a gas flowing direction and has a multistage structure.

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Claim 33 (new): The gas pressure regulator according to claim 25, wherein both sides of the electrochemical cell serving as gas partition wall have closed vessels, wherein one side serves as a high pressure gas tank and an opposite side is connected to a gas consuming system, a pressure sensor is disposed in a closed vessel in the opposite side and wherein a pressure sensor interlocks with a relay switch connected between both the first and second electrodes of the electrochemical cell to compensate for the consumption of gas.

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Claim 34 (new): The gas pressure regulator according to claim 25, wherein the electrochemical cell functions as a gas refining filter.

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Claim 35 (new): The gas pressure regulator according to claim 25, wherein the ion conductor is a proton conductor, wherein the proton conductor is formed with a derivative by introducing a proton dissociation group to carbon atoms forming at least type of material selected from a group consisting of fullerene molecules, a cluster having carbon atoms as a main component and a structural body having tubular or linear carbons, and wherein the proton generated in the first electrode is moved to the second electrode through the proton conductor.

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Claim 36 (new): The gas pressure regulator according to claim 35, wherein the proton dissociation group is -XH where X indicates an arbitrary atom or an atomic group having bivalent bonds and H indicates a hydrogen atom.

5

Claim 37 (new): The gas pressure regulator according to claim 36, wherein the proton dissociation group is -OH or -YOH where Y indicates an arbitrary atom or an atom group having bivalent bonds.

10 Claim 38 (new): The gas pressure regulator according to claim 37, wherein the proton dissociation group is selected from the group consisting of -OH, -OSO₃H, -COOH, -SO₃H, -OPO(OH)₂, and -C₆H₄-SO₃H.

15 Claim 39 (new): The gas pressure regulator according to claim 35, wherein the fullerene molecules are a spherical shell type carbon cluster molecule C_m where m indicates a natural number in which C_m may form a spherical shell structure.

20 Claim 40 (new): An electrochemical device comprising:
an electrochemical cell including a first electrode for decomposing a hydrogen gas into one or more protons, a second electrode for converting the protons generated in the first electrode into the hydrogen gas again and a proton conductor sandwiched in between both the electrodes;

25 a high pressure vessel disposed in a first electrode side of the electrochemical cell to accommodate a gaseous material including the hydrogen gas; and

30 a gas consuming part including a pressure reducing part in which the electrochemical cell functions to reduce pressure in the high pressure vessel, a hydrogen gas storage part disposed in contact with a second electrode side in the pressure reducing part, a third electrode disposed in contact with the hydrogen storage part to decompose the hydrogen gas supplied from the hydrogen gas storage

part into protons; a fourth electrode for converting the protons generated in the third electrode into water, and a proton conductor sandwiched in between both the electrodes wherein the protons is converted into water in the fourth electrode to remove electrochemical energy between the third electrode and the fourth electrode.

Claim 41 (new): The electrochemical device according to claim 40, wherein an oxygen gas or an oxygen containing gas is supplied to a surface of the fourth electrode that does not contact the proton conductor to react with the protons passing through the proton conductor and convert the protons into water, and wherein the electrochemical energy is removed between the third electrode and the fourth electrode.

Claim 42 (new): A gas storage device comprising:
a gas inlet and outlet part for introducing or discharging gas;
a gas storage part for storing gas; and
an electrochemical cell disposed in the gas storage part and including a first electrode for decomposing the gas into ions, a second electrode for converting the ions generated in the first electrode into the gas again and an ion conductor sandwiched in between both the electrodes wherein the gas is supplied to or discharged from the gas storage part through the gas inlet and outlet part in accordance with the function of the electrochemical cell to decrease or increase pressure in the gas storage part.

Claim 43 (new): The gas storage device according to claim 42, further comprising a gas storage assist system, the gas storage assist system including:
a gas passage for supplying the gas to the gas inlet and outlet part provided in the gas storage device;
a pressure detecting member for detecting gas pressure in the gas passage;
a voltage detecting member for detecting voltage generated between the first electrode and the second electrode;

a calculating member for calculating a control current signal on the basis of the gas pressure and the voltage;

a current supply member for generating a control current; and

a switching member for alternately switching a state such that the control
5 current is supplied between the first electrode and the second electrode and a state such that the voltage is detected until the voltage reaches a predetermined value.

Claim 44 (new): A method for regulating a gas pressure comprising:
decomposing gas into ions in a first electrode;

10 conducting the decomposed ions to a second electrode side through an ion conductor sandwiched in between the first electrode and the second electrode; and
converting the conducted ions to the gas again in the second electrode.

Claim 45 (new): The method according to claim 44, wherein a control
15 current is supplied to both ends of the first electrode and the second electrode to control a quantity of the control current so that a flow rate of gas flows across both the electrodes.

Claim 46 (new): The method according to claim 44, wherein an
20 electrochemical cell including the first electrode, the second electrode and the ion conductor serves as a gas partition wall and when a pressure difference is generated at both sides of the electrochemical cell, a potential between both the electrodes is controlled to regulate the pressure.

25 Claim 47 (new): The method according to claim 46, wherein an electromotive force generated from a pressure difference is short-circuited or a pressure is regulated by a variable resistor.

Claim 48 (new): The method according to claim 46, wherein a high
30 pressure gas storage tank is disposed at one side of the electrochemical cell serving as the gas partition wall and a closed vessel connected to a gas consuming system is

disposed at the other side, wherein a pressure sensor is disposed in the closed vessel in another side, and wherein the pressure sensor interlocks with a relay switch connected between both the first and second electrodes of the electrochemical cell to compensate for the consumption of gas.

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REMARKS

The present amendment makes editorial changes and corrects typographical errors in the specification, which includes the Abstract, in order to conform the specification to the requirements of United States Patent Practice. No new matter is added thereby.

In addition, the present amendment cancels original claims 1-24 in favor of new claims 25-48. Claims 25-48 have been presented solely because the revisions by red-lining and underlining which would have been necessary in claims 1-24 in order to present those claims in accordance with preferred United States Patent Practice would have been too extensive, and thus would have been too burdensome. The present amendment is intended for clarification purposes only and not for substantial reasons related to patentability pursuant to 35 U.S.C. §§ 101, 102, 103 or 112. Indeed, the cancellation of claims 1-24 does not constitute an intent on the part of the Applicants to surrender or disclaim any claimed subject matter.

Early and favorable consideration on the merits is respectfully requested.

Respectfully submitted,

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